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THE HALF-LIFE, NEUTRON CAPTURE AND FISSION CROSS-SECTIONS OF LONG LIVED EINSTEINIUM-254

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(*Received* 27 *May* 1957)

Abstract—The half-life of long lived ^{254}E has been found to be 480 $\pm$ 70 days. A measurement of the burn-up of ^{254}E gave a reactor neutron destruction cross-section of 2700 $\pm$ 600 barns. No ^{253}Fm, in equilibrium with ^{253}E was detected after the irradiation, so that the reactor neutron capture cross-section of ^{254}E is less than 40 barns.

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Two isomeric states of ^{254}E exist; one decays mainly by β^- emission to ^{254}Fm with a 39 hr period, and the other with a much longer half-life decays to ^{250}Bk by emitting 6·42 MeV α-particles.[1,2] It has been suggested that the latter is the ground state of ^{254}E and that the short lived isomer is a metastable state.[1] The half-life, neutron capture and fission cross-sections of the long lived state are of practical importance quite apart from their intrinsic interest, because this is the longest lived state of einsteinium and is an attractive target material for further irradiations.

The first published value of the half-life of the long lived state was >2 years,[1] and subsequently we reported a value of 320 days.[2] We have continued to observe the decay of this source as long as it was practicable, and now report the result of the measurement to supplement our earlier value, since it may be some time before we can re-determine the half-life with new material.

The long lived state of ^{254}E was produced by the prolonged, high intensity neutron irradiation of plutonium previously described.[2] After chemical separation a source of einsteinium was sublimed in vacuum on to a polished platinum disk. Within 2 months after the end of the plutonium irradiation 6·42 MeV α-particles could be resolved from the 6·63 MeV α-particles of ^{253}E, using a gridded ionization chamber and 30 channel pulse height analyser. The decay of the 6·42 MeV α-particle peak was followed for 500 days and gave a half-life of 480 $\pm$ 70 days. The error is large because the counting rate was low and corrections for the counter background and the low energy tail of the ^{253}E α-pulse distribution had to be made. Nevertheless, this result is more accurate than that reported earlier.[2]

The cross-sections of 480-day ^{254}E were determined by irradiating 140 α-disintegration per hour (about 10^{-15} g) of ^{254}E as einsteinium chloride in a sealed quartz capsule in the Materials Testing Reactor, Idaho, for 21 days; the integrated neutron

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§ The Knolls Atomic Power Laboratory is operated by the General Electric Company for the U.S. Atomic Energy Commission under Contract No. W-31-109 Eng. 52.

[1] B. G. HARVEY, S. G. THOMPSON, G. R. CHOPPIN and A. GHIORSO *Phys. Rev.* **99**, 337 (1955).
[2] M. JONES, R. P. SCHUMAN, J. P. BUTLER, G. COWPER, T. A. EASTWOOD and H. G. JACKSON *Phys. Rev.* **102**, 203 (1956).

flux was $4{\cdot}6 \times 10^{20}$ n cm^{-2}. In such an irradiation the important nuclear reactions are:

$$E^{254} \xrightarrow{(n,\gamma)} E^{255} \xrightarrow[24\ \text{days}]{\beta^-} Fm^{255} \xrightarrow[21{\cdot}5\ \text{hr}]{\alpha}$$

E^{254} → fission; E^{255} → capture

At the end of the irradiation, after a delay period to allow the ^{255}Fm formed during the irradiation period to decay and fresh ^{255}Fm to come into equilibrium with its parent ^{255}E, the capsule was opened and the contents quantitatively removed. The products of the irradiation plus Cf tracer were separated using ion exchange techniques.[2] Alpha counting and α-pulse analyses showed that 30 d.p.h of ^{254}E were recovered. Assuming that the losses in loading the quartz capsule before irradiation and unloading and chemical processing of the ^{254}E after irradiation were 25 per cent, the recovered amount of ^{254}E corresponds to a yield of 40 d.p.h at the end of the irradiation. No ^{255}Fm was found with the irradiated ^{254}E so that we can set an upper limit of 6 d.p.h for the yield of ^{255}Fm. Using 40 barns for the capture cross-section of ^{255}E,[3] these measurements give a pile neutron destruction cross-section of 2700 ± 600 barns and a pile neutron capture cross-section of <40 barns for ^{254}E. Clearly, in an experiment of this type where there was no tracer to give the chemical yield, the resulting cross-sections depend upon the estimate of the losses. Past experience has shown that the assumed value of 25 per cent is reasonable. Furthermore, the error of 600 barns in the fission cross-section allows for an uncertainty of 20 per cent in the assumed losses, as well as the errors in the flux and counting. It is interesting to note that the total cross-section is about that predicted from systematics[4] although the neutron fission and capture cross-sections might be expected to be more nearly equal.[5]

We acknowledge with pleasure the assistance of Mr. A. S. RICHARDSON at the MTR, who arranged for the irradiation.

[3] University of California Radiation Laboratory. *Unclassified Report UCRL-2944.*
[4] B. G. HARVEY *Phys. Rev.* **99,** 333 (1955).
[5] J. R. HUIZENGA *U.N. Geneva Conference Proceedings* **2,** 208 (1955).

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CHEMICAL EFFECTS IN FISSION PRODUCT RECOIL—II

THE DECOMPOSITION OF URANYL IODATE

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(*Received* 15 *May* 1957)

Abstract—Under pile irradiation uranyl iodate decomposes, elementary iodine being formed. The amount of decomposition is proportional to the number of fissions that occur; the *G* factor is 5·8 iodine atoms per 100 eV of recoil energy absorbed. A constant proportion (14 per cent) of the ^{131}I formed in fission is extracted with the reduced iodine, irrespective of the extent of decomposition. This is interpreted as the result of the chemical reaction involving the primary fission fragment and its surroundings.

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IN the first paper of this series[1] the chemical effects of recoiling fission fragments, and their final chemical condition, were studied by irradiating a ground mixture of the fissile and target materials, uranium oxide and potassium iodate respectively. The principal difficulty in the estimation of decomposition as a function of energy expended in the fission process was the uncertainty in the fraction of the fission fragment recoil energy actually expended in the iodate phase. This problem would not exist in a homogeneous system, e.g. a uranium compound, and to obtain results comparable with those of the above work the pile irradiation decomposition of uranyl iodate has been studied.

The investigation of the solid state decomposition of a compound such as an iodate is complicated by the fact that the products need not necessarily be stable on dissolution. They may conceivably react with water, with the excess iodate, or with one another, and the apparent yield could thus be considerably distorted. Fortunately such reactions do not occur in this case to any great extent. The only decomposed species apparent when the iodate was dissolved was elementary iodine (as was expected, the solution being slightly acid) and evidence was obtained which demonstrated that elementary iodine was in fact the predominant species before the iodate was dissolved.

EXPERIMENTAL

Uranyl iodate monohydrate was prepared by adding iodic acid to a solution of uranyl nitrate. The sparingly soluble yellow powder was thoroughly washed with water, recrystallized from very dilute nitric acid and washed again following the procedure of RICHARDS and MERIGOLD.[2] Analysis for uranium (ignition to U_3O_8 at 800–900°C) and for iodate (reduction with acidified potassium iodide and titration with sodium thiosulphate) gave the results U = 37·3 per cent, I = 39·6 per cent; calculated values for $UO_2(IO_3)_2.H_2O$ are U = 37·3 per cent, I = 39·8 per cent.

Samples of weight 0·5 g were sealed, in air, in silica capsules and irradiated in BEPO in holes of nominal flux $1{\cdot}4 \times 10^{12}$ neutrons cm^{-2} sec^{-1}, for periods ranging from 3 min to 6 hr. Other samples were sealed in evacuated glass capsules and similarly irradiated for periods of up to 22 hr. After about 2 weeks the capsules were broken into a flask containing carbon tetrachloride and sodium hexametaphosphate solution, and the flask was then shaken vigorously for about 30 min.

As uranyl iodate is only slightly soluble in water it was found convenient to use a complexing

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(1) G. N. WALTON and I. F. CROALL *J. inorg. nucl. Chem.* **1**, 149 (1955).
(2) T. W. RICHARDS and B. S. MERIGOLD *Z. anorg. Chem.* **31**, 245 (1902).

reagent as solvent. Sodium hexametaphosphate did not interfere with subsequent operations and in preliminary tests was found to be efficient. It did not, however, readily dissolve the irradiated compound, owing to the formation of a protective layer of iodine on the surface of the particles. This had first to be removed, and the above procedure proved effective. The pH of the hexametaphosphate solution was about 4·5, similar to the natural pH of the saturated iodate solution, and the resulting iodine species were elementary iodine and iodate in the carbon tetrachloride and aqueous phases respectively.

The two phases were separated, diluted to standard volume and analysed, the iodine colorimetrically with a Hilger "Spekker" absorptiometer, using a filter transmitting in the region 0·52–0·58 μ, the iodate by reduction with iodide and titration with thiosulphate. Aliquots of each phase were then purified radiochemically by repeated extraction of iodine into sulphurous acid, followed

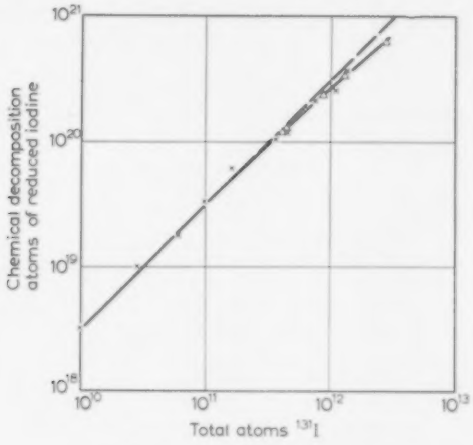


FIG. 1.—Chemical decomposition.
△—sample evacuated.
×—sample not evacuated

by oxidation with nitrous acid and back-extraction into carbon tetrachloride. After 24 hr ^{131}I was counted in a halogen-filled liquid counter as the carbon tetrachloride solution, and the chemical yield determined by colorimetric analysis of the same solution. This procedure necessarily imposed a reasonably low concentration limit on the counting solutions, and no self-absorption corrections were considered necessary.

Selected samples were converted to silver iodide and their decay followed for periods of up to 50 days. No deviation from 8·0 day half-life was observed. Aluminium absorption curves were plotted for other samples as a check on radiochemical purity.

A solution of ^{131}I as potassium iodide, of known activity, supplied by Isotopes Division AERE, was quantitatively oxidized and extracted into carbon tetrachloride. The liquid counter was calibrated with this solution, and the disintegration rates of the various samples determined. These were corrected for decay, and the original number of ^{131}I atoms obtained.

RESULTS

In Fig. 1 the number of atoms of reduced iodine observed is plotted against the total number of ^{131}I atoms, the latter being proportional to the number of fissions. The relationship is linear for small doses, with a yield of $3{\cdot}14 \times 10^{8}$ iodine atoms per atom ^{131}I. A falling away from linearity becomes apparent at about 6 per cent decomposition ($5{\cdot}7 \times 10^{19}$ atoms of reduced iodine) when the amount of decomposition becomes comparable to the total amount of iodate present initially. In the longest irradiation 65 per cent decomposition has occurred. Potassium iodate shows no

decomposition detectable under comparable conditions[1] and the effect was assumed to be entirely due to fission. Assuming the fission yield for mass 131 to be 3·0 per cent[3] then $9{\cdot}4 \times 10^6$ atoms of reduced iodine were observed per fission event.

It may be seen from Fig. 1 that the results for the evacuated and non-evacuated samples lie on the same curve. The rate of fission was 50 per cent lower for the evacuated samples, due to absorption of thermal neutrons by the glass capsule, and it does not appear that either oxygen over-pressure or fission rate has any significant effect.

IDENTITY OF THE DECOMPOSITION PRODUCT

Experiments were performed in which samples of uranyl iodate, irradiated for 1 hr, were washed with solvent before dissolution. Results were somewhat variable but it was found that about 30 per cent of the total yield of reduced iodine distilled as

TABLE 1

	I_2 extracted (mg)	Percentage I_2 extracted	Specific activity (arbitrary units)	Percentage activity extracted
Sample 23				
Total CCl_4 wash	13·9	74	24	18
Aqueous wash*	4·7	25	212	54
Extracted on dissolution	0·2	1	3100	28
Iodate			56	
Sample 29				
Iodine distilled from iodate	6·7	32	12	6
Successive CCl_4 washes				
1	2·7		24	5
2	2·8		47	10
3	1·3		53	5
4	0·9		60	4
Total CCl_4 wash	7·7	36		24
Extracted on dissolution	6·7	32	136	70

* In the aqueous wash 1–2 per cent of the iodine was present as iodide.

elementary iodine on to the walls of the container, and that a further 40 per cent could be removed from the powder by shaking with carbon tetrachloride. The time necessary for this varied, being sometimes as little as 20 min and at other times several hours. If the iodate was then shaken with water a total of 99 per cent of the iodine was removed, without substantial dissolution having occurred. (The solubility of uranyl iodate is ca. 0·1 per cent at room temperature.[4]) The results of typical experiments are shown in Table 1. Almost the whole of the reduced iodine must be located at or very near to the surface of the particles, and a large proportion of it is obviously elementary. It was postulated that the entire yield was elementary iodine which, being uninhibited by electrostatic forces, diffused rapidly under the influence

[3] A. C. PAPPAS *M.I.T. Laboratory for Nuclear Science, Technical Report No.* 63 (1953).
[4] P. ARTMANN *Z. anorg. Chem.* **79**, 327 (1912).

of the pile radiation to the particle surface. The possibility that a small percentage of the product may be some other species was not rigidly excluded, but the following observations support the above hypothesis.

(a) Owing to the hydrolysis of the uranyl ion an aqueous solution of the iodate is acidic, and it was to be expected that iodine removed by the aqueous wash would appear mainly as the element. However, a saturated solution of the iodate in 10 per cent disodium phosphate solution has a pH of 7·7; it is too alkaline to oxidize iodide and in fact hydrolyses iodine. When irradiated uranyl iodate, previously washed with carbon tetrachloride, was shaken for a short time with 10 per cent sodium diphosphate solution, much of the iodine was again observed to be elementary.

(b) When a sample of uranyl iodate was first irradiated in the pile and then exposed to ^{60}Co γ-rays (24 hr at 3700 r min^{-1}) the proportion of iodine removable by carbon tetrachloride increased (Table 2). It was shown that this dose did not cause any further decomposition.

TABLE 2

	I_2 removed by CCl_4 washing (mg)	Total I_2 (mg)	Percentage removed
γ-irradiated fraction	2·7	7·9	34
Control fraction	1·6	8·4	18

These figures do not include that iodine which distilled from the powder. This sample was irradiated in the pile for 2·5 hr at a flux of 6×10^{11} neutrons cm^{-2} sec^{-1}, higher flux positions not being available at the time; i.e. the diffusion appears to be flux dependent.

(c) Uranyl iodate is a yellow powder which becomes dark brown on irradiation. The combined wash with carbon tetrachloride and water, which removes 99 per cent of the iodine, restores the yellow colour. Neither solvent used separately has this effect. Although substances frequently darken in colour on irradiation it would appear more reasonable to assume that in this case the colour is due to iodine.

It should be noted that if any periodate had been formed by a recombination process it would not have been detected.

THE *G* FACTOR

It would appear from the above that no significant reaction involving the decomposition products occurs on dissolution, and the yield of $9·4 \times 10^6$ atoms of iodine per fission does in fact represent $9·4 \times 10^6$ iodate ions decomposed.

In an average fission event 195 MeV of energy are released, as shown in Table 3.[5] It may be supposed that the recoil energy and much of the β-energy will be absorbed by the sample, but that the more penetrating radiations will mainly escape. Little error should be introduced by assuming that the decomposition is entirely due to the recoil effect, and the *G* factor is then 5·8 iodate ions decomposed per 100 eV absorbed. This is in close agreement with the value of 5·6 previously obtained for potassium iodate,[1] although too much significance should not be attached to this. Lattice stability must be an important factor in any such solid state effect, i.e. the

[5] S. GLASSTONE and M. C. EDLUND *The Elements of Nuclear Reactor Theory* p. 71. D. Van Nostrand, New York (1952).

decomposition of an anion may vary with the cation, as has been shown for nitrates.[6] However, in the previous study which was made on a mixture of uranium oxide and potassium iodate it was necessary to assume the fraction of the energy of the fragments recoiling from the oxide that was expended in the iodate. It would appear that the estimate made, viz. one third, was not seriously in error.

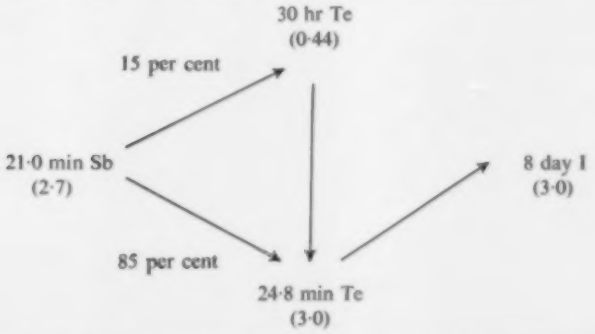
TABLE 3.—ENERGY LIBERATED IN THERMAL FISSION OF ^{235}U

	MeV
Kinetic energy of recoiling fission fragments	162
β-decay energy of fission fragments	5
γ-decay energy of fission fragments	5
Energy of fission neutrons	6
Instantaneous γ-ray energy	6
Neutrino energy	11

DISTRIBUTION OF ^{131}I

From Table 1 it may be seen that the specific activity of the iodine which distilled from the iodate was relatively very low. Successive CCl_4 washes produced solutions of steadily increasing specific activity, while that of the small amount of iodine not removable by washing was much higher. As the diffusion process continually

TABLE 4.—MASS 131 DECAY CHAIN



The total individual fission yields are given in parenthesis.

separates the iodine from the fissile phase it would produce an effect of this nature, but this would not be expected to be as pronounced. It should, however, be remembered that iodine is not a primary fission fragment in the 131 mass chain, and that decay to form iodine involves appreciable delay, as shown in Table 4.[7] If those species, which on decay form elementary iodine, do not diffuse, then this delay would considerably amplify the above effect.

It is also possible that a substantial fraction of the activity which extracts on

[6] G. HENNIG, R. LEES and M. S. MATHESON *J. chem. Phys.* **21**, 665 (1953).
[7] J. BLOMEKE *O.R.N.L. Report No.* 1783 (1955).

dissolution with the reduced iodine was present as an ionic species which does not diffuse. It has been shown that this is not so for the reduced iodine itself, but there is no *a priori* reason for assuming the same to hold for the fission product iodine. An indication that a water-soluble species of higher specific activity than the element

TABLE 5

	I_2 extracted (mg)	Percentage I_2 extracted	Specific activity (arbitrary units)	Percentage activity extracted
Aqueous wash	10·2	75	117	49
CCl_4 wash	3·2	24	92	12
Extracted on dissolution	0·2	1	4600	39
Iodate			77	

did exist was obtained when an irradiated uranyl iodate sample was washed first with water and then with carbon tetrachloride. Reference to Table 5 shows that in this case the latter wash did not produce the greater specific activity (compare Table 1).

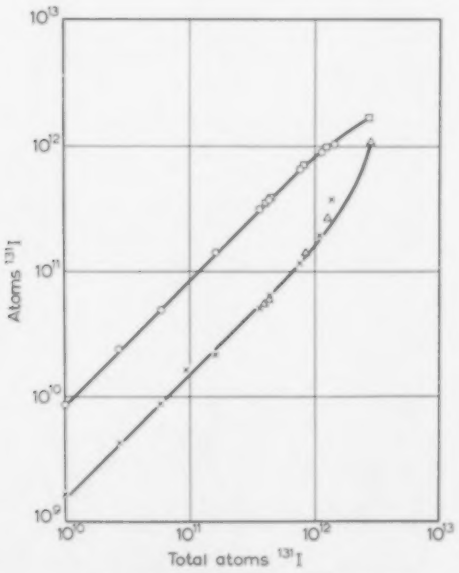


FIG. 2.—Distribution of ^{131}I activity.
△—reduced iodine, sample evacuated.
×—reduced iodine, sample not evacuated.
□—iodate, sample evacuated.
○—iodate, sample not evacuated.

The distribution of ^{131}I between the reduced iodine and the undecomposed iodate was constant (Fig. 2) i.e. it was independent of the extent of decomposition. Deviations were observed only for the longer irradiations in which gross decomposition had occurred. As both the number of iodine atoms and the activity associated

with them were proportional to the number of fissions that occurred, the specific activity of the reduced iodine was constant. For short irradiations the specific activity of the iodate would be linearly dependent on the number of fissions. These effects are illustrated in Fig. 3.

A similarly constant distribution was observed with potassium iodate,[1] and as it was noted that the specific activity of the iodine was always higher than that of the iodate it was postulated that the mechanism was isotopic exchange. In a solid lattice exchange would be expected to occur only between near neighbours, and it is the composition in the immediate environment of the fission fragment, rather than in the

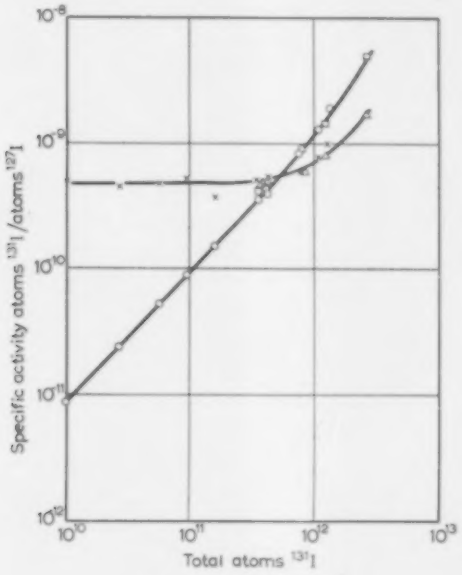


FIG. 3.—Specific activity.
△—reduced iodine, sample evacuated.
×—reduced iodine, sample not evacuated.
□—iodate, sample evacuated.
○—iodate, sample not evacuated

crystal as a whole, which controls the distribution. The decomposition in this region will be almost entirely the result of the arrest of the particular fragment concerned, i.e. will be effectively independent of the bulk decomposition.

However, in this work the iodate specific activity exceeds that of the iodine for the longer irradiations, giving a cross-over effect (Fig. 3) which is quite inconsistent with any exchange mechanism. Moreover some of the irradiations were short compared with the delay in formation of iodine by decay of the primary fragments (Table 4), and under such conditions radiation-induced exchange would not lead to a constant distribution.

The exchange mechanism was not unequivocally established for potassium iodate, and it would seem reasonable to assume that the observed effects had a similar cause in each case, particularly as approximately the same fraction of the activity is extracted with the reduced iodine, 14 per cent with uranyl iodate and 11 per cent with potassium iodate. It was noted that these figures are similar to the fraction of the decay chain,

15 per cent, which proceeds via the transition between the tellurium isomers (Table 4). The soft γ-rays emitted during an isomeric transition are often highly converted internally, and this frequently results in the disruption of the ion or molecule involved.[8] If the primary fission fragments were incorporated in an oxy-ion which persisted during the subsequent β-decay, eventually forming an iodate (or periodate) ion,

TABLE 6

	Specific activity of iodate (arbitrary units)
Sample 38	
γ-irradiated fraction	810
Control fraction	822
Sample 39	
Heated fraction	799
Control fraction	785

but which frequently did not survive the isomeric transition, then the observed result would be obtained. Essentially the same postulate was put forward previously[1] but was discarded as at the time it was not known that 85 per cent of ^{131}Sb disintegrations lead directly to the tellurium ground state.

Assuming the various constants given in Table 4, the variation with time of the

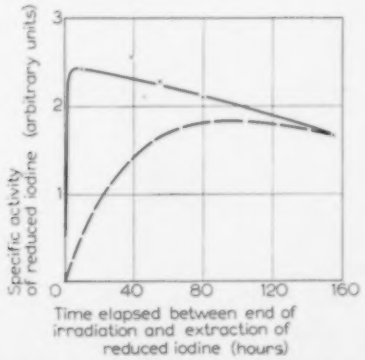


FIG. 4.—Variation with time of the specific activity of the reduced iodine, following a 1 hr irradiation. The various values are normalized to coincide at 155 hr.
— × — × — specific activity assuming the association of ^{131}I with the reduced iodine is independent of the mode of tellurium decay.
— — — specific activity assuming the association of ^{131}I with reduced iodine is dependent the decay of $^{131\,m}$Te only.
⊗ experimental values.

specific activity of the iodine, subsequent to a 1 hr irradiation, was calculated, as expected for the above mechanism. For the first few days this differs markedly from the same function calculated on the assumption that the iodine activity is independent of the path of decay, as shown in Fig. 4. Several samples of uranyl iodate were then

[8] R. R. WILLIAMS *The Fission Products National Nuclear Energy Series* Vol. IV, Paper 18, p. 9. McGraw-Hill, New York.

irradiated for 1 hr, and at varying times afterwards these were dissolved, and the iodine extracted and immediately radiochemically purified. After a further period such that in all 14 days had elapsed since irradiation, they were repurified (to remove ^{133}Xe) and counted. Decay corrections were then made so as to give the activity of each iodine sample at the time of separation from its tellurium parents. These specific activities, plotted in Fig. 4, indicate quite clearly that the reduced iodine activity is not particularly associated with the isomeric transition. Moreover evidence has recently appeared [9,10] suggesting that a considerable fraction of the ^{131m}Te disintegrations do not involve the transition but lead directly to ^{131}I. This would then destroy the numerical coincidence which caused the above mechanism to receive serious consideration.

Numerous studies[11,12,13] have been made of the distribution of activity following neutron capture by the central atom of an oxy-ion. It has been shown that the retention of activity (as the oxy-ion) can be increased by subsequent heating or γ-irradiation, and that after a substantial neutron dose the observed retention may be much greater than for zero dose. It has also been shown that this is not an exchange effect but is due to the recombination of fragments of the original ion.[14] A similar mechanism might well be operative in this case, but in view of the changing chemical character of the 131 atom (as a result of β-decay) it is difficult to predict exactly how the retention would vary with dose. It is most improbable, however, that it would be constant. Moreover, two pile irradiated samples were respectively exposed to ^{60}Co γ-radiation ($5{\cdot}3 \times 10^6$ r) and heated to 200°C for 24 hr. The iodate activity was unaffected (Table 6) and it was concluded that such recombination effects are not important.

An explanation which is consistent with all the above observations would be to regard the distribution as the result of the chemical reaction between the fission fragment and its surroundings, occurring immediately the atom comes to rest. The primary fission fragment and possibly excited atoms and radicals produced during its arrest would be involved, and it is not possible to predict what species would be formed, nor is it known what chemical transformations might result from the subsequent β-disintegrations. The proportion of the ^{131}I that would be extracted with the reduced iodine cannot then be predicted, but this would be expected to be constant, independent of both the time of irradiation and the specific activities of the various species. Only gross decomposition, such that there was an appreciable probability of a fragment coming to rest in a previously decomposed region, would affect the reaction and hence the distribution. This picture is analogous to that proposed by WILLARD and co-workers[15] to explain similar retention effects in organic halides.

Acknowledgement—The author wishes to express his gratitude for many valuable discussions with Mr. G. N. WALTON.

[9] E. HEBB *Phys. Rev.* **97**, 987 (1955).
[10] C. A. MALLMANN, A. H. W. ATEN, D. R. BES and C. M. DE MCMILLAN *Phys. Rev.* **99**, 7 (1955).
[11] J. W. COBBLE and G. E. BOYD *J. Amer. chem. Soc.* **74**, 1282 (1952).
[12] R. E. CLEARY, W. H. HAMILL and R. R. WILLIAMS *J. Amer. chem. Soc.* **74**, 4675, (1952).
[13] J. H. GREEN, G. HARBOTTLE and A. G. MADDOCK *Trans. Faraday Soc.* **49**, 1413 (1953).
[14] A. G. MADDOCK and M. M. DE MAINE *Canad. J. Chem.* **34**, 275 (1956).
[15] J. E. WILLARD *Ann. Rev. nucl. Sci.* **3**, 193 (1953).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 12 to 13. Pergamon Press Ltd., London

INFRA-RED SPECTRA OF OSMIUM–NITROGEN COMPOUNDS

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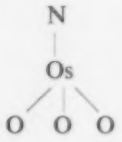
Abstract—Infra-red spectra of potassium osmiamate, $K[OsO_3N]$ and potassium nitrilopentachloro-osmate, $K_2[OsCl_5N]$ have been measured and the Os–N stretching frequency identified by the use of ^{15}N.

DURING investigations on infra-red spectra of nitric oxide complexes of transition metals,[1] the opportunity has been taken to measure the spectra of compounds containing Os–N bonds. The spectrum (Fig. 1a) of $K[OsO_3N]$ confirms the structure of the ion



as a distorted tetrahedron; this structure was based on chemical evidence[2] and on X-ray diffraction studies.[3] In agreement with this structure, there are two strong bands at 858 and 890 cm^{-1}, attributable to Os–O stretching modes, which lie in the region of the Os–O frequency of 953 cm^{-1} observed in osmium tetroxide.[4] Whilst the Os–O frequencies are at lower frequencies in $K[OsO_3N]$ compared to OsO_4, other osmium–oxygen complexes, e.g. $K_2OsO_3(NO_2)_23H_2O$, show bands in the same region; this shift is compatible with a decrease in the multiple bond character of the Os–O link.

A third strong, sharp band at 1023 cm^{-1} is observed with $K[OsO_3N]$. This band has been shown to be due to the Os–N vibration, since the spectrum of the osmiamate prepared from ammonium nitrate enriched in ^{15}N showed a well defined isotope effect (Fig. 1b), an additional strong band being observed at 992 cm^{-1} in this case; the expected shift for a band at 1023 cm^{-1} due to an Os–N vibration would be to 991 cm^{-1}.

In potassium nitrilopentachloro-osmate, $K_2[OsCl_5N]$, the only band observed in the 700–1100 cm^{-1} region occurs at 1073 cm^{-1}; this band again shows an isotope shift in the ^{15}N containing compound, a second band then being found at 1041 cm^{-1} (calculated 1039 cm^{-1}).

The rather high frequency of the Os–N vibrations in these compounds suggests that the Os–N bond has considerable multiple bond character and is a quite strong one, which is in keeping with the considerable chemical stability[2] of the compounds.

[1] J. LEWIS and G. WILKINSON Unpublished work.
[2] N. V. SIDGWICK *The Chemical Elements and their Compounds* Vol. II, pp. 1503, 1507. Oxford (1950).
[3] F. M. JAEGER and J. E. ZANSTRA *Proc. Acad. Amst.* **35**, 610 (1932).
[4] L. A. WOODWARD and H. L. ROBERTS *Trans. Faraday Soc.* **52**, 615 (1956).

It may be noted that we have confirmed a previous observation[5] and observed by mass spectrometric analysis that only nitrogen is formed on thermal decomposition of $K[OsO_3N]$; no oxides of nitrogen could be detected.

The osmiamate and the nitrilopentachloro-osmate are both diamagnetic over a range 80–293°K. In the case of the last-named salt, this implies that spin pairing occurs in the ion, due, perhaps, to d^4sp^3 hybridization, since the compound would be expected otherwise to be paramagnetic with two unpaired electrons.

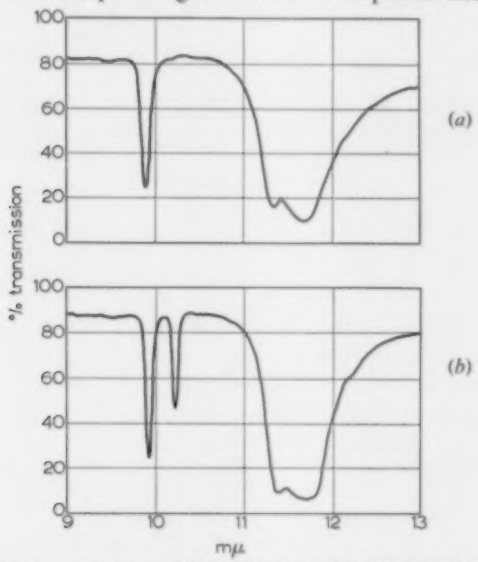


FIG. 1.—Infra-red spectrum of (A) $K[OsO_3N]$, (B) $K[OsO_3{}^{15}N]$, in Nujol.

EXPERIMENTAL

$K[OsO_3N]$ and $K_2[OsCl_5N]$ were prepared by WERNER's methods.[6] The ^{15}N-containing compounds were prepared from $^{15}NH_4NO_3$ enriched to 30·7 per cent ^{15}N. Mass analyses of the nitrogen in the osmiamate showed no change in the isotopic ratio. $K_2OsO_3(NO_2)_23H_2O$ was prepared by the method of WINTREBERT.[7]

Infra-red spectra were taken in Nujol mulls and using a Perkin–Elmer Model 21 instrument with NaCl optics. The following bands were observed:

$K[OsO_3N]$	1023 (*s*, sharp)	890 (*s*)	858 (*s*)	
$K[OsO_3{}^{15}N]$	1023 (*s*, sharp)	992 (*s*, sharp)	890 (*s*)	858 (*s*)
$K_2[OsCl_5N]$	1073 (*s*, sharp)			
$K_2[OsCl_5{}^{15}N]$	1073 (*s*, sharp)	1041 (*s*, sharp)		

$K_2OsO_3(NO_2)_23H_2O$. 1633 (*s*, H_2O), 1400 (*s*, NO_2), 1380 (*s*,NO_2), 1344 (*m*, NO_2), 1331 (*s*, NO_2), 882 (*m*, NO_2?), 850, 840 (*s*, Os–O), 831, 825 (*s*, NO_2?).

Acknowledgements—We are indebted to Dr. E. R. ROBERTS for a gift of enriched ammonium nitrate and for the use of the mass spectrometer, and to the Chemical Society for a grant for the purchase of osmium tetroxide.

[5] A. JOLY *C.R. Acad. Sci., Paris* **112**, 1443 (1891).
[6] A. WERNER and K. DINKLAGE *Ber. dtsch. chem. Ges.* **34**, 2698 (1901).
[7] L. WINTREBERT *Ann. Chim. (Phys.)* **28** (vii), 54, 86 (1903).

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PREPARATION OF BERYLLIUM FLUORIDE FROM BERYLLIA

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Abstract—The preparation of beryllium fluoride from two samples of beryllia (calcined at 500 and 1400°C) by treatment with anhydrous hydrogen fluoride has been studied in relation to temperature and time of reaction. The optimum temperature is about 220°C, and the amount converted, which may be as high as 98·4 per cent, does not increase appreciably after 1 hr. X-ray analysis has given no evidence for solid solution formation between BeF_2 and unreacted BeO.

BERYLLIA is a suitable compound for use in a reactor as a component of the fuel element, as a reflector, or as a moderator.[1] The conversion of insoluble beryllia to water-soluble beryllium fluoride by treatment with hydrofluoric acid or other fluorinating agents is a possible stage in the chemical processing of beryllia-moderated fuels.

It has been reported that BeO is inert towards most materials, except HF.[1] The most commonly used methods for the preparation of BeF_2 have been described by EMELÉUS,[2] e.g. the action of aqueous HF on beryllia or beryllium carbide. Alternatively, it can be prepared by the decomposition of the double fluoride, ammonium fluoberyllate $(NH_4)_2BeF_4$ in a stream of CO_2[3] or in a graphite retort at 850°C,[4] although in the latter case, BeF_2 is produced in a finely divided state and has a great tendency to hydrolyse. The treatment of beryllia alone with anhydrous HF does not appear to have been investigated in any detail. ADAMOLI[5] describes the use of gaseous HF to fluorinate BeO at 700–750°C. However, details of the purity of the product are not given, and also BeF_2 is appreciably volatile at elevated temperatures (vapour pressure at 900°C $\approx$ 15 mm). Accordingly, experiments were performed on the hydrofluorination and fluorination of beryllia to determine the optimum conversion conditions. Gas–solid reactions of beryllia with anhydrous hydrofluoric acid, fluorine and chlorine trifluoride were studied in relation to reaction temperature, time, and particle size. In addition, beryllia and beryllium metal were dissolved in aqueous HF, and beryllium was treated with fluorine.

EXPERIMENTAL AND MATERIALS

Two samples of powdered beryllia prepared by calcination of the hydroxide at 500 and 1400°C were studied. The major impurities in these samples were Na (900 p.p.m.) and Ca, Al and Mg (150 p.p.m.). The HF and ClF_3 gases used were

* Australian Atomic Energy Commission.

(1) *Reactor Handbook Materials: General Properties, U.S. Atomic Energy Commission* p. 41. McGraw-Hill, New York (1955).
(2) H. J. EMELÉUS *Fluorine Chemistry* (Edited by J. H. SIMONS). Vol. 1, p. 34 Academic Press, New York (1950).
(3) P. LEBEAU *C.R. Acad Sci., Paris* **126**, 1418 (1898).
(4) L. J. DEREHAM and D. A. TEMPLE *Symposium on the Extraction Metallurgy of some of the Less Common Metals, Institution of Mining and Metallurgy, London.* Paper No. 18 (March 1956).
(5) C. ADAMOLI U.S. Pat. 2,303,783 (Dec. 1942).

obtained from I.C.I. cylinders in thermostatically controlled baths operating at 35°C, and fluorine gas from a 10 A, 10 V generator. Gas flow-rates were maintained at 15 ml/min for HF, and 5 ml/min for F_2 and ClF_3. In view of the toxic character of beryllium compounds, all operations involving the production of BeF_2 from BeO were performed inside an α-type glove box. The experimental techniques of gaseous hydrofluorination and fluorination using nickel reaction furnaces were identical with those previously described.[6] Surface areas were measured by the B.E.T. nitrogen-adsorption method.

The BeF_2 samples were analysed for fluorine content by pyrohydrolysis at 1000°C in a silica apparatus.[7,8] WARF, CLIVE and TEVEBAUGH[8] found that light metal fluorides are very slowly pyrohydrolysed in steam at 1000°C, but, if mixed with an accelerator such as U_3O_8, the reaction is complete in the presence of air in a short time, producing the metal diuranate. Experience has shown that no appreciable pyrohydrolysis of BeF_2 took place at temperatures <900°C, but above this temperature the evolution of HF was rapid. When U_3O_8 was added, the HF was liberated at a much lower temperature (600°C), with an increased rate of evolution, and gave fluorine contents 2–5 per cent higher than when BeF_2 was pyrohydrolysed alone. The fluorine figures quoted (to ±0·1 per cent) are those obtained using U_3O_8. X-ray powder diffraction photographs were obtained by the Debye–Scherrer technique and also by the use of a Guinier-type focusing camera.[9] Debye–Scherrer samples were sealed into thin-walled Pyrex capillary tubes in the usual way. Samples for the Guinier camera were mounted on Sellotape and sealed from atmospheric water-vapour by a second piece of Sellotape.[9]

RESULTS AND DISCUSSION

The results of dry-way hydrofluorination of the two BeO samples are shown in Table 1.

Table 2 shows the surface areas of the two samples and the products of hydrofluorination at 225°C for 3 hr.

Typical results of dry-way fluorination of beryllia and beryllium are presented in Table 3.

The digestion of beryllia with 40 per cent aqueous HF at 80°C for 90 min, followed by evaporation and drying at 130°C for 16 hr, gave a product with a fluorine content of 72·4 per cent; this was increased to 78·3 per cent by heating at 400°C for 4 hr. At 80°C the dissolution of beryllium in 40 per cent aqueous HF was rapid, giving a product having a fluorine content of 77·4 per cent after drying which, however, decreased to 73·5 per cent after heating at 500°C for 6 hr.

These results show that maximum conversion is obtained at about 220°C for both the 500 and 1400°C calcined beryllia, and also that hydrofluorination times >1 hr give no marked increase in the yield. The widely differing surface areas of the two samples have no effect on the conversion, but an elevenfold decrease in surface area occurs for the 500°C calcined sample after hydrofluorination, whilst virtually no change occurs with the 1400°C calcined sample. The dissolution of both

[6] K. R. HYDE and D. J. O'CONNOR *Nucleonics* **15**, No. 1, 68 (1957).
[7] G. M. GILLIES, N. J. KEEN, B. A. J. LISTER and D. REES Atomic Energy Research Establishment C/M 225 (1954).
[8] J. C. WARF, W. D. CLIVE and R. P. TEVEBAUGH *Analyt. Chem.* **26**, 342 (1954).
[9] R. W. M. D'EYE Atomic Energy Research Establishment C/R 1524 (1954).

TABLE 1.—DRY-WAY HYDROFLUORINATION OF BeO

BeO calcination temperature (°C)	Hydrofluorination temperature (°C)	Hydrofluorination time (hr)	Per cent F in product (F in BeF_2 = 80·85 per cent)
500	225	0·5	69·9
	225	3	73·7
	225	3	79·5
	600	3	62·0
1400	150	4	52·3
	200	4	70·2, 71·0
	225	0·67	65·5
	225*	3	68·7
	225	4	73·0
	225	3	61·5
	225	3	73·7
	250	6	59·6
	225*	3	66·0
	300	3	56·9
	400	3	34·4
	400	4	39·1
	500	2	33·5
	600	3	50·0

* Water-insoluble residue from previous hydrofluorination.

TABLE 2.—SURFACE AREA OF BeO BEFORE AND AFTER HYDROFLUORINATION

Sample	Surface area (m^2/g)	
	500°C calcined	1400°C calcined
BeO	273	8·7
Product of hydrofluorination at 225°C for 3 hr	24·3 (98·4 per cent BeF_2)	9·9 (85 per cent BeF_2)

TABLE 3.—FLUORINATION OF BeO AND Be

Sample	Fluorination			Per cent F in product (F in BeF_2 = 80·85 per cent)
	Gas	Temperature (°C)	Time (hr)	
BeO (1400°C calcined)	F_2	210	3	8·1
	ClF_3	200	3	12·5
	ClF_3	600	3	44·3
Be metal	F_2	400	3	9·3

beryllia and beryllium in 40 per cent aqueous HF, followed by evaporation of the excess HF, produced BeF_2 samples with a high F content. This is at variance with statements in the literature regarding the hydroscopic and hydrolytic nature of BeF_2.[2,4] However, conversions using gaseous F_2 or ClF_3 are not as efficient, no water being produced in the reaction.

The polymorphism of beryllium fluoride has been reviewed by KIRKIN, NOVOSELOVA and SIMANOV,[10] and by ROY, ROY and OSBOURNE,[11] who emphasized the striking similarity to silicon dioxide. Beryllium and fluorine are similar in ionic size and polarization properties to silicon and oxygen, and in consequence SiO_2 and BeF_2 form similar crystal structures, although the formal ionic charges in BeF_2 are only half those in SiO_2. BeF_2 prepared by thermal decomposition of ammonium fluoroberyllate has a tetragonal structure analogous to the low-temperature form of cristobalite. At 130°C this is transformed into a cubic structure corresponding to the high-temperature form of cristobalite. The phase which exists in equilibrium with liquid BeF_2 is hexagonal and analogous to quartz. Both the low and high temperature forms have been observed. The transformation temperature is 220°C. If liquid BeF_2 is rapidly quenched a vitreous form is obtained.

Samples prepared by gaseous hydrofluorination of beryllia at 225°C were found to consist of some unchanged BeO and the low-temperature quartz form of BeF_2. Those samples prepared by dissolving beryllia or beryllium metal in aqueous HF, evaporation and calcination at 500°C in air contained only the low-temperature-quartz form of BeF_2. Presumably the high-temperature modification is formed in the primary crystallization process and this is transformed into the low-temperature form on cooling.

Table 4 compares the observed $\sin^2\theta$ values for a sample prepared by the aqueous

TABLE 4.—MEASURED AND CALCULATED $\sin^2\theta$ VALUES FOR BeF_2

I_{obs}	*hkil*	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.
M+	1010	0·0350	0·0350
S	1011	0·0570	0·0571
M+	1120	0·1051	0·1051
M+	1012	0·1231	0·1232
M+	1121	0·1273	0·1272
M	2021	0·1624	0·1622
W	1122	0·1934	0·1933
W	0003	0·1984	0·1984
M−	2022	0·2281	0·2283
M−	1013	0·2230	0·2234
W	2130	0·2453	0·2453
M−	2131	0·2671	0·2673
W	1123	0·3032	0·3035
M−	2132	0·3332	0·3334
M− } D	3031	0·3380 }	0·3374
W }	1124	0·3386 }	0·3385

M = medium, S = strong, W = weak, D = diffuse

[10] D. F. KIRKIN, A. V. NOVOSELOVA and Y. P. SIMANOV *Dokl. Akad. Nauk, SSSR* **107**, 837 (1956).
[11] D. M. ROY, R. ROY and E. F. OSBOURNE *J. Amer. ceramic Soc.* **36**, 185 (1953).

HF route with those calculated for a hexagonal unit cell with $a = 4{\cdot}742$ kx $\pm$ 0·010 kx and $c = 5{\cdot}178$ kx $\pm$ 0·010 kx. These may be compared with the values $a = 4{\cdot}72$ kx and $c = 5{\cdot}18$ kx quoted for the low-temperature quartz form.[10] No difference in unit cell dimensions between pure beryllia and the beryllia in partially hydrofluorinated material could be detected on 19 cm Debye–Scherrer photographs, where a change of 0·02 per cent would be detectable in well crystalline samples of this type. It appears therefore that no appreciable solid solubility of BeF_2 in Be had occurred.

CONCLUSIONS

Treatment of beryllia with anhydrous hydrogen fluoride at 220°C, or 40 per cent hydrofluoric acid followed by evaporation to dryness, gives better than 90 per cent conversion to beryllium fluoride. It may be possible to obtain quantitative conversion by the use of fluidized bed techniques. X-ray analysis of hydrofluorinated BeO shows no evidence of solid solution of BeO in BeF_2 and confirms previously published data.

Acknowledgement—Our thanks are due to Miss P. BARTLETT for performing the pyrohydrolysis analyses.

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THE ELECTRICAL PROPERTIES OF URANIUM OXIDES*

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Abstract—The electrical conductivity and thermoelectric power of uranium oxides in the UO_2—U_3O_7 range have been studied at temperatures between 27 and 400°C after annealing at various elevated temperatures. The following compounds were identified: UO_{2+x}, a metal-deficit semiconductor; U_4O_{9-y}, a metal-excess semiconductor; and U_3O_{7-z}, a metal-excess semiconductor. The presence of all major phases was confirmed by X-ray powder techniques. An energy of about 0·4 eV is required to free a positive carrier from the interstitial oxygen in UO_{2+x}. In U_4O_9 or U_3O_7 the energy required to free an electron from the hexavalent uranium varies from 0·4 eV at high carrier concentrations to 0·9 eV at the lower concentrations.

The electrical properties of the oxides are interpreted in terms of the phase relationships of the UO_2–U_3O_7 system and certain modifications of existing phase diagrams are suggested.

THE electrical conductivity of the oxides of uranium has been studied by many investigators[1–11] and the results of their work have been summarized by MEYER[12] and by KATZ and RABINOWITCH.[13] The oxides UO_3 and U_3O_8 are reported to be metal-excess semiconductors, while UO_2 is said to be an amphoteric semiconductor. The conductivity of UO_3 at room temperature is very low; the reported values range from 10^{-7} to less than 10^{-8} $(\Omega\ cm)^{-1}$. Part of the conductivity of U_3O_8 is ionic in nature. The reported values, which include both the ionic and electronic contributions to the conductivity, vary from 2×10^{-4} to 1×10^{-7} $(\Omega\ cm)^{-1}$. In UO_2 conductivity values ranging from 3×10^{-1} to 4×10^{-8} $(\Omega\ cm)^{-1}$ have been measured at 27°C. The ranges of conductivity are, of course, caused by variations in the composition, purity, apparent density, and crystalline perfection of the specimens studied.

The studies of MEYER and co-workers,[1–3] of CHIOTTI,[4] and of HARTMANN[5] on UO_2 probably are the most significant. MEYER studied the electrical conductivity of UO_2 as a function of temperature to determine "activation energies" for free carriers in samples of widely different conductivities, and obtained values ranging from 0·3 to 0·9 eV. CHIOTTI also studied the conductivity of UO_2 as a function of temperature, but extended the measurements to higher temperatures where intrinsic conductivity becomes predominant.

HARTMANN pointed out that the increase of electrical conductivity with the addition of oxygen makes UO_2 a metal-deficit semiconductor in which the current carriers are positive holes. He confirmed this hypothesis by Hall-coefficient measurements. His specimen has a conductivity of 0·013 $(\Omega\ cm)^{-1}$ and a Hall coefficient of 770 cm^3/C.

* Work performed under AEC Contract W-7405-eng 92.

(1) W. MEYER *Z. Phys.* **85,** 278 (1933).
(2) W. MEYER and H. BERG *Tech. wiss. Abh. Osram* **3,** 96 (1934).
(3) W. MEYER and H. NELDEL *Z. Tech. Phys.* **18,** 588 (1937).
(4) P. CHIOTTI CT-1985 (4 January 1945).
(5) W. HARTMANN *Z. Phys.* **102,** 709 (1936).
(6) M. LEBLANC and H. SACHSE *Ber. sachs. Ges. (Akad.) Wiss.* **82,** 155 (1931).
(7) M. LEBLANC and H. SACHSE *Physik. Z.* **32,** 887 (1931).
(8) E. FRIEDERICH and L. SITTIG *Z. anorg. Chem.* **145,** 127 (1925).
(9) E. FRIEDERICH *Z. Phys.* **31,** 813 (1925); **34,** 637 (1925).
(10) W. AMREIN *Schweiz. Arch angew. Wiss.* **8,** 85 (1942).
(11) J. PRIGENT *J. Phys. radium.* **10,** 58 (1949).
(12) W. MEYER *Z. Elektrochem.* **50,** 274 (1944).
(13) J. J. KATZ and E. RABINOWITCH *The Chemistry of Uranium. National Nuclear Energy Series,* Div. VIII, Vol. 5. McGraw-Hill, New York (1951).

These data can be interpreted to give a free-carrier concentration of 1×10^{16} positive holes per cm^3 and a mobility of 10 cm^2 per V sec.

In most of these investigations only one or two specimens were studied. The purity and excess oxygen content were not known. The type of conductivity (electron or positive hole) was not determined, nor was the possibility of the existence of several phases considered. It, therefore, seemed of interest to the authors to extend the work on UO_2 and carefully consider more of the factors involved in producing different conductivities and activation energies in UO_2.

EXPERIMENTAL WORK

During the course of this investigation, it was found necessary to study the electrical properties of UO_2 produced by several different processes. Both sintered and non-sintered specimens were studied. Since the electrical properties of UO_2 were found to be dependent upon its past history, a detailed description of the preparation of samples will be deferred until the electrical properties of a particular sample are discussed. However, most of the specimens studied were prepared from normal MCW (Mallinckrodt Chemical Works) UO_2 powder and were isostatically pressed at 100,000 lb/in^2 (without a binder) into cylindrical rods about $\frac{1}{4}$ by 4 in. These rods were sintered in a hydrogen atmosphere at 1650 or 2050°C for 1 hr. Specimens for electrical measurements were cut from the rods either before or after sintering.

Spectrographic analysis of these materials indicated the metallic impurity content to be very low, a few parts per million at most. Because of the rather high excess oxygen content of the samples, it was assumed that the effect of the metallic impurities was negligible. Oxygen/uranium ratios were calculated from the weight gain on ignition of the UO_2 powder to U_3O_8.

After the electrical measurements were completed on a particular sample, the phases were determined by X-ray techniques, in most cases.

The specimens for electrical measurements were lapped to $\frac{1}{8}$ by $\frac{1}{4}$ by $\frac{1}{2}$ in. on silicon carbide paper. They were mounted in a Lavite holder constructed so that electrical contact could be made on the ends and one face of the sample. The end contacts were Chromel plates to which were welded Chromel-Alumel thermocouples. The thermocouple wires also were used as current leads and thermoelectric-power probes. The contacts on the face of the sample were platinum beads and served as conductivity probes. All contacts were spring loaded.

Conductivities were measured by comparing the potential drop between the probes with the potential drop across a standard resistor. The voltages were measured with a Leeds and Northrup K-2 potentiometer. The use of potential probes insured against contact-resistance errors. The accuracy of the measurement was limited by the effect of grain boundaries and by the degree of homogeneity of the sample.

Measured conductivities (σ_m) were converted to "corrected" conductivities (σ_c) by the expression:[14]

$$\sigma_c = \left(1 + \frac{P}{1 - P^{2/3}}\right)\sigma_m \qquad (1)$$

where P represents the volume pore fraction of the sample calculated from the ratio of the actual density of the sample to the theoretical density of UO_2. The conductivities were referred to the theoretical density of UO_2 because the excess oxygen was

[14] H. W. RUSSELL *J. Amer. ceram. Soc.* **18**, 1 (1935).

determined on a weight-per cent basis, whereas the conductivity depends on the number of carriers per unit volume. This correction made it possible to compare the conductivity of specimens of different densities. However, caution must be exercised in any quantitative interpretation of the data because of the effects of grain boundaries.

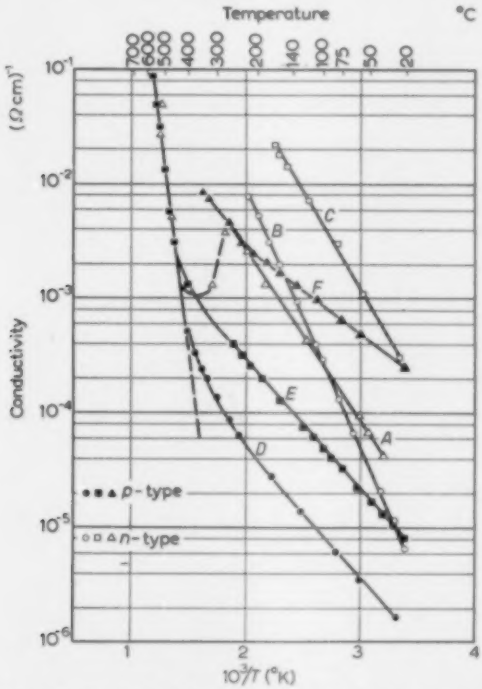

FIG. 1.—Conductivity of sintered specimens of *n*- and *p*-type UO_2.

The thermoelectric power was determined by establishing a thermal gradient along the specimen and measuring the thermal e.m.f. generated. The thermal gradient was produced by a heater containing two windings which could be controlled separately. The thermoelectric power was measured with respect to the Chromel leg of the thermocouples in contact with the ends of the specimen. To obtain the absolute thermoelectric power, the value for Chromel was subtracted, algebraically, from the measured thermal e.m.f./°C. Thermal e.m.f. of the sample and thermocouples were measured with a Leeds and Northrup K-2 potentiometer. The accuracy of the value obtained for the thermoelectric power was limited by the precision with which the difference in temperature at the ends of the specimen was determined (a relatively large gradient, 15 to 20°C, was employed) and by the homogeneity of the sample.

During the measurements as a function of temperature the holder was enclosed in a Vycor tube and connected to a vacuum system at a pressure of about 10^{-3} mm Hg. Room temperature measurements were made in air at atmospheric pressure.

CHARACTERISTICS OF SINTERED SPECIMENS

The initial data were obtained using a 3 in. rod of MCW UO_2, which had been sintered for 1 hr at 2050°C in a hydrogen atmosphere, and are represented in Fig. 1

by the open triangles on curve *A*. After sintering, the oxygen–uranium ratio was found by ignition analysis to be 2·011 ± 0·005 and the density of the rod was 86 per cent of the theoretical value. During the temperature cycle the rod was in a measurement chamber under vacuum (~10^{-5} mm Hg). Of particular interest is the anomaly occurring between 200 and 350°C (represented by the broken portion of the curve). The general shape of this curve could be duplicated, but the magnitude of the conductivity changed slightly during several temperature cycles.

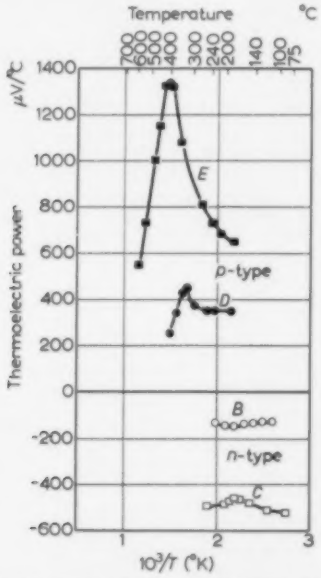

FIG. 2.—Thermoelectric power of sintered specimens of *n*- and *p*-type UO_2.

The other curves of Fig. 1 and those of Fig. 2 were obtained on specimens ⅛ by ¼ by ½ in. cut from the original rod. These measurements also were made under vacuum (10^{-3} mm Hg). The measurements on the *n*-type specimen, represented by the open circles and squares on curves *B* and *C* were reproducible, as indicated by the data for several temperature cycles between 20 and 200°C. When these samples were heated above 200°C, the conductivity decreased in the same anomalous manner as the conductivity of the rod, curve *A*, and the thermoelectric power became *p*-type. As the temperature was increased to 400°C, where the intrinsic conductivity became apparent, the thermoelectric power again became *n*-type. However, when the temperature subsequently was reduced the extrinsic conductivity was *p*-type and additional measurements of conductivity as a function of temperature resulted in the data shown by curve *D* in Fig. 1 and 2.

Additional temperature cycling for several days increased the extrinsic *p*-type conductivity and resulted in the properties shown by the curves *E* and *F* of Fig. 1 and 2. Evidently a small amount of oxygen was absorbed above 200°C, even though the measurements were carried out in a vacuum of about 10^{-3} mm Hg. When a vacuum of 10^{-5} mm Hg was used, it appears that a negligible amount of oxygen was absorbed. Thus, the anomaly seems to be caused by a reversible phase change in

which the conductivity changes from *n*-type to *p*-type. Also, the anomaly can be eliminated by the addition of a very small amount of oxygen into the lattice, which makes the material *p*-type throughout the extrinsic region.

The appearance of *n*-type conductivity was rather surprising, since the oxygen/uranium ratio of 2·011 ± 0·005 indicated about 3×10^{20} excess oxygen atoms per cm^3, and interstitial oxygen atoms in UO_2 are associated with positive conduction. If the oxygen content had been below the stoicheiometric ratio 2·00, then the negative carriers could be supplied by the excess uranium atoms. Also, in view of the anomalous decrease in conductivity with increasing temperature above 200°C, the *n*-type conductivity seems to be explained only by assuming the presence of excess uranium in a phase other than UO_2.

It is readily apparent from Fig. 1 that the curves of log conductivity as a function of reciprocal temperature, in general, consist of two straight lines and that the conductivity of each portion can be fitted to an expression of the type

$$\sigma = Ae^{-\Delta E/2kT} \tag{2}$$

where:

σ is the conductivity,
A is a constant,
k is Boltzmann's constant,
ΔE is the energy necessary to free a charge carrier,
T is the Kelvin temperature.

The application of this equation to the conductivity at high temperatures is of particular significance. This portion of the curves appeared to be reproducible, regardless of the behaviour of the conductivity at low temperatures. Therefore, it is reasonable to suppose that the high-temperature portions of the curves of Fig. 1 represent the intrinsic conductivity of UO_2. Assuming intrinsic conductivity is present, a value of 3 eV was calculated for the energy-band separation in uranium dioxide from the slope of the curve and equation 2.

Recent studies of the optical absorption of UO_2 films indicate a region of strong absorption at about 2·7 eV and an absorption edge at about 5 eV.[15] The absorption at 2·7 eV corresponds roughly to the value of 3 eV calculated from the temperature dependence of the conductivity, whereas the absorption edge at 5 eV indicates a higher energy band separation for UO_2. It could be assumed that the absorption at 2·7 eV is caused by an impurity level but the magnitude of the conductivity would then require the number of impurities to be greater than the number of atoms in the UO_2 lattice. Also, the change of thermoelectric power from positive to negative at the higher temperatures is difficult to understand if the absorption is due to an impurity. On the other hand, approximate calculations based on the measured conductivity and reasonable values for the mobility and effective mass of the charge carriers suggest that the energy band separation is less than 3·0 eV. The conductivity of these specimens of UO_2 were much higher than would be expected if the band separation of the compound was 3 or 5 eV. These apparent discrepancies can, perhaps, be resolved through precise measurements of conductivities and carrier mobilities in single crystals, and additional work on the optical absorption of UO_2.

The low-temperature portions of the curves of Fig. 1 also reveal some interesting

[15] G. H. Winslow, R. J. Thorn and R. J. Ackermann *Bull. Amer. phys. Soc.* **1**, Ser. II, No. 7, 341 (1956).

characteristics. A rather large difference in the slopes of the *n*- and *p*-type curves is obvious. Applying equation 2 to the extrinsic portions of Fig. 1 gives activation energies of about 0·9 eV for *n*-type carriers and about 0·4 eV for positive carriers. It also is interesting to note that the extrinsic slope of curve *A* (open triangles) lies between these values.

The thermoelectric power of this specimen (curve *E*, Fig. 2) poses a difficult problem. Simple theory predicts a thermoelectric power which decreases with

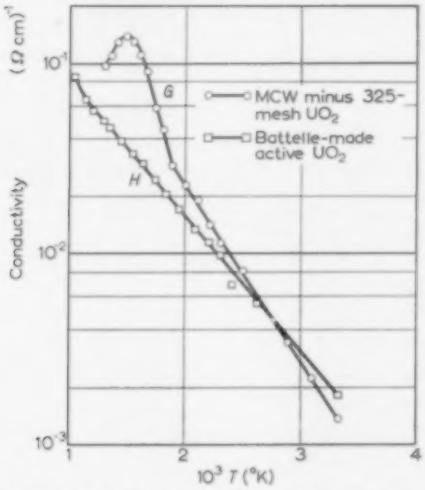

FIG. 3.—Conductivity of sintered specimens of UO_2 of various histories.

increasing temperature for a temperature-dependent population of current carriers. This obviously is not the case for the *p*-type curves in which an initial sharp rise in thermoelectric power (although the conductivity increases) was observed. Even the *n*-type curves are relatively flat and do not decrease as would be expected.

Some further measurements on the electrical properties of sintered specimens of uranium dioxide are shown in Fig. 3 and 4. These measurements were made on:

(1) A specimen (curve *G*, open circles) cut from a rod of regular MCW minus 325 mesh UO_2, sintered in hydrogen for 1 hr at 1600°C to 79 per cent of theoretical density.

(2) A specimen (curve *H*, open rectangles) cut from a rod of Battelle made "active" UO_2,* sintered in hydrogen for 1 hr at 1600°C to 95 per cent of theoretical density. The measurements were made under a pressure of about 10^{-3} mm Hg.

Figs. 3 and 4 are of particular interest since they compare the electrical properties of a specimen of UO_2 which sintered to high density with those of a specimen which sintered to the usual density (about 80 per cent of theoretical). The conductivity curves display a remarkable difference at the higher temperatures. The anomaly in the electrical conductivity as the temperature is increased, noted for the previous sample, is obvious on the conductivity curve of the normal UO_2 (curve *G*), but does not appear on the curve of the active material (curve *H*). Even the slopes of the two

* Sinterable to high density.

curves of conductivity versus temperature are significantly different, that of the normal MCW specimen being 0·36 eV at the lower temperatures and changing to 0·84 eV above 200°C, while that of the active specimen was 0·28 eV.

An examination of the thermoelectric-power curves (Fig. 4) also reveals some interesting differences. Although the curves are somewhat similar in general shape, there is a large difference in the magnitudes of the thermoelectric power, even though the conductivities are nearly identical. Again the increase of thermoelectric power with increasing carrier concentration is to be noted. The shape of these curves was reproducible but the magnitudes changed on further temperature cycling.

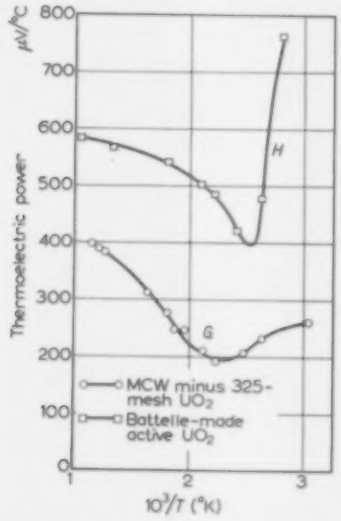

FIG. 4.—Thermoelectric power of sintered specimens of UO_2 of various histories.

An explanation of the differences in Fig. 3 and 4 is rather difficult to advance. If it is assumed that the anomaly in the conductivity curve of the normal specimen was due to a phase change, the transition is clearly lacking in the active specimen. The question then is, why does not the active material change phases at higher temperatures. A possible answer to this question might be the presence of an impurity. The starting material for preparation of both normal and active UO_2 is uranyl nitrate, which is decomposed to UO_3 and finally reduced by hydrogen to UO_2. The difference in the materials is that in the case of the active material the UO_3 is ball milled, thoroughly washed, and then reduced to produce the active UO_2. If any nitrates persist through the decomposition, they probably are removed by the washing. Thus it is possible that the normal UO_2 may contain nitrogen impurities absent in the active material. But even if nitrogen is present in the normal material, it is not understood how it could cause UO_2 to undergo a phase change at elevated temperatures.

ANNEAL AND QUENCH EXPERIMENTS

The electrical properties of non-sintered specimens of a wider range of oxygen content also were measured, in addition to those of the sintered specimens described in the previous section. The non-sintered specimens were prepared by exposing

normal MCW minus 325-mesh UO_2 powder (Lot No. 77016, oxygen–uranium ratio = 2·032) to dry oxygen for various lengths of time at 180°C. Care was taken to exclude nitrogen from the system. After the exposure, oxygen assays were made on the materials by ignition analysis. The powders were then hydrostatically pressed under 100,000 lb/in² without a binder into cylindrical rods. The density of the rods was about 60 per cent of the theoretical density of UO_2.

Room-temperature measurements on the "as-prepared" specimens revealed that all were *p*-type and that the conductivity rose slightly in a linear fashion with increasing oxygen content (see curve *A*, Fig. 5). However, the conductivity did not increase so

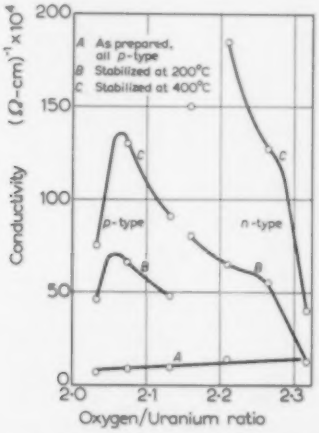

FIG. 5.—Room-temperature conductivity as a function of oxygen/uranium ratio of pressed specimens of UO_2.

rapidly with excess oxygen content as might be expected, indicating that the specimens were non-homogeneous. Microscopic examination of the powders revealed that oxygen was concentrated on the surface of the granules (as evidenced by the colour of the granules) and was not distributed throughout the crystal lattice. Therefore, these specimens were subjected to extensive annealing treatments in order to insure homogeneity.

For annealing, the specimens were sealed in small Vycor capsules under a residual pressure of dry argon. A temperature, 200°C, slightly above the temperature of preparation was chosen for the initial anneal. To study the changes of electrical properties occurring during the anneal, the specimens were quenched periodically by dropping into an oil bath, then removed from the capsules and their electrical properties measured at room temperature.

The largest changes of electrical properties occurred during the first 16 hr at 200°C. Conductivities increased by nearly an order of magnitude and some of the specimens (of relatively high oxygen content) became *n*-type. Thereafter the room-temperature conductivities (measured at 16 hr intervals) of all specimens continued to increase slowly until a steady state was reached. Steady state was attained after about 60 hr at 200°C for *p*-type specimens and after about 80 hr for *n*-type specimens. There were no further changes in type of conductivity.

The *n*-type conductivity exhibited by these specimens confirmed the extrinsic electronic conductivity in part of the UO_2–U_3O_7 system indicated by the measurements on sintered specimens. Thus, along with the simple process of homogenization

there must be postulated an ordering process during the anneal in which the bonding orbitals in the lattice of UO_2 are affected (increase in conductivity) and in which a new phase or phases appear (appearance of *n*-type conductivity). The occurrence of such a process was later verified by X-ray measurements in which changes in lattice constant and crystal structure were observed.

By plotting the steady-state values of the conductivities obtained by annealing at 200°C as a function of oxygen content, curve *B* of Fig. 5 was obtained. It can be seen that as oxygen is added up to an oxygen–uranium ratio of about 2·06, the *p*-type conductivity of UO_2 increases. Beyond this point the conductivity begins to decrease with increasing oxygen content. Finally, between the oxygen–uranium ratios of 2·13 to 2·16 the conductivity becomes *n*-type. Between the *p*- and *n*-type branches of curve *B* there appears to be a discontinuity. Further increasing oxygen content results in decreasing *n*-type conductivity.

The specimens used above also were annealed at 400°C. Periodic measurement of the room-temperature conductivities revealed an orderly increase of conductivity with time until a new steady state was reached. This occurred between 30 and 40 hr for all specimens. The steady-state values of conductivity after annealing at 400°C are shown by curve *C*, Fig. 5, which is similar in shape to curve *B* but displaced to much higher values of conductivity. Attention is called to the specimen of oxygen/uranium ratio of 2·160. After annealing at 200°C the specimen was *n*-type; however, it became *p*-type when annealed at 400°C and the conductivity fits on neither branch of curve *C*.

The anneal-quench experiments were also performed at temperatures of 600, 800, and 1000°C. At these higher temperatures considerable oxygen was lost from the specimens so that a quantitative description of the behaviour of the specimens was not possible. However, indications were that annealing up to 800°C followed by quenching to room temperature resulted in further increases of room-temperature conductivity and that curves similar to curves *B* and *C*, Fig. 5 could be plotted. No further changes of type of conductivity were noted for these specimens. Annealing above 800°C seemed to have little effect on the magnitude of the conductivity but loss of oxygen may have masked the effects of annealing.

The data shown in Fig. 5 give considerable information on the phase relationships in the UO_2–U_3O_7 system. If the end points of the branches of the curves are extrapolated to zero conductivity, they are found to intersect the composition axis close to oxygen/uranium ratios corresponding to the formulas UO_2 and U_3O_7. X-ray analysis of the specimens of high oxygen/uranium ratios (2·264 and, especially 2·317) revealed that the specimens consisted of a tetragonal phase whose pattern corresponded to that reported for U_3O_7. The UO_2 phase was, of course, verified at the lower oxygen contents. Furthermore, the behaviour of the conductivity of the specimens of intermediate oxygen/uranium ratio strongly indicates the presence of an additional phase. X-ray analysis of these specimens revealed that they consisted of UO_2 or U_3O_7 and considerable amounts of a cubic structure corresponding to the formula U_4O_9.

Because of the electrical behaviour of the phases found in the UO_2–U_3O_7 system they can be identified as:

(1) UO_{2+x}, a metal-deficit semiconductor;
(2) U_4O_{9-y}, a metal-excess semiconductor;
(3) U_3O_{7-z}, a metal-excess semiconductor.

The presence of metal-deficit phases of U_4O_9 and U_3O_7 was not detected by these

experiments, yet their existence should not be excluded. Electrical measurements on specimens with oxygen/uranium ratios slightly above 2·250 and 2·333 would perhaps confirm their existence. One specimen with an oxygen/uranium ratio above that of U_3O_7 was investigated. It had an oxygen/uranium ratio of 2·353 and after annealing at 400°C was *n*-type. Since a phase corresponding to U_3O_{7+x} would be *p*-type, this specimen was clearly a metal-excess phase of some higher oxide of uranium. From X-ray data the new phase was identified as U_3O_8.

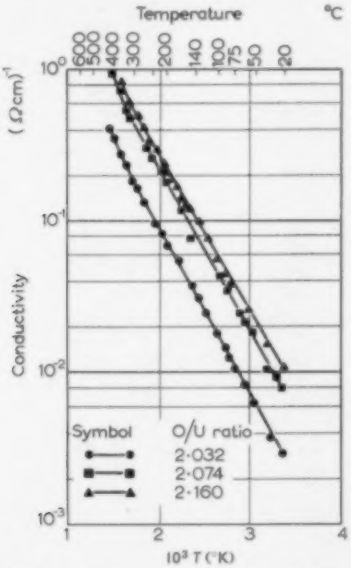

FIG. 6.—Conductivity of pressed specimens of *p*-type UO_2 of various oxygen/uranium ratios after annealing at 400°C and quenching to room temperature.

New specimens were cut from the original rods and their electrical properties were determined as a function of temperature after annealing at 400°C for 100 hr. The electrical measurements were not extended to above 400°C, in order to minimize the loss or gain of oxygen in the measuring apparatus.

In Figs. 6 and 7 is plotted the behaviour of the conductivity of the *p*- and *n*-type specimens, respectively, as a function of reciprocal temperature. These curves represent the extrinsic behaviour of typical pressed specimens in the UO_2–U_3O_7 system and are to be compared with the extrinsic portion of the curves of Figs. 1 and 3. In general, corresponding to their higher oxygen content, the pressed specimens have somewhat higher conductivities than the sintered specimens. The slopes of the pressed *p*-type specimens are comparable to those of the *p*-type sintered specimens, but there is considerable difference between the *n*-type slopes of Fig. 1 and those of Fig. 7.

The thermoelectric power of the pressed specimens (Fig. 8) can be compared with the data shown in Figs. 2 and 4. The decrease in thermoelectric power with increasing temperature and conductivity for the *p*-type samples in Fig. 8 corresponds more closely to that predicted by simple theory. The thermoelectric power of the pressed specimen of oxygen/uranium ratio 2·160 is especially interesting in that it duplicates the results of the anneal–quench experiments. The double crossover corresponds,

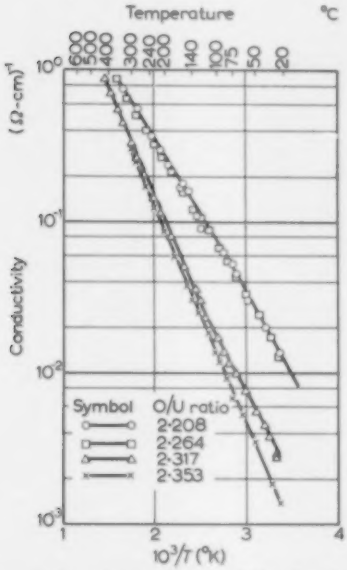

FIG. 7.—Conductivity of pressed specimens of *n*-type UO_2 of various oxygen/uranium ratios after annealing at 400°C and quenching to room temperature.

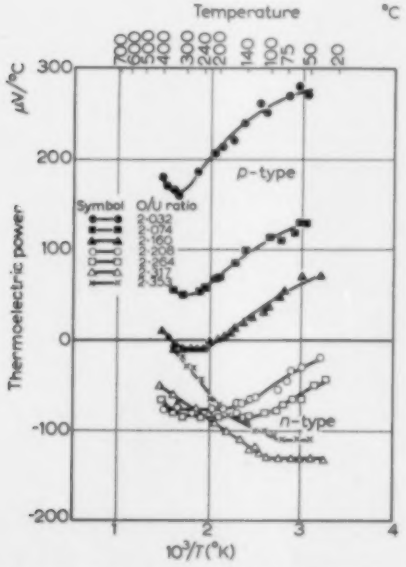

FIG. 8.—Thermoelectric power of pressed specimens of UO_2 of various oxygen uranium ratios after annealing at 400°C and quenching to room temperature.

probably, to the transitions:

$$A\ UO_{2+x} + B\ U_4O_9 \rightarrow \underset{(p\text{-type})}{C\ UO_{2+x'}} + \underset{(n\text{-type})}{D\ U_4O_{9-y}}$$

$$\rightarrow \underset{(p\text{-type})}{E\ UO_{2+x'}} + F\ U_4O_{9-y'}.$$

The first *p*-type characteristic was quenched in from above 400°C. As the temperature was raised to about 200°C the ratio of UO_{2+x} to U_4O_{9-y} was changed until U_4O_{9-y}, *n*-type, was predominant. The ratio of the two phases changed continuously with further increases of temperature, with the formation of UO_{2+x} being favoured. Finally, at about 335°C, *p*-type conductivity was again predominant and the specimen was in a state similar to that originally quenched in.

DISCUSSION

The UO_2—U_3O_7 *System*

Because of the complexities of the reaction between oxygen and uranium, many investigators of the oxygen–uranium system have found it difficult to obtain reproducible results. Among the most reliable of the phase diagrams of the UO_2—U_3O_7 system are those published by PERIO[16] and GRONVALD.[17] Although agreeing in general, the phase diagrams presented by these investigators differ in detail. A careful study of Figs. 5–8 of this report suggests certain further modifications of the published diagrams within the region studied. These modifications, illustrated in Fig. 9, may be summarized as follows:

(1) At 180°C and above, oxygen is soluble in the UO_2 lattice up to an oxygen/uranium ratio of about 2·06. This is indicated by the linear dependence of electrical conductivity with oxygen content within this region. At higher oxygen content, the bonding and structure are affected and a second phase, U_4O_9, appears.

(2) A two-phase region above 180°C of $UO_2 + U_4O_9$ extends to a composition of $UO_{2\cdot24}$. The exact representation of this region depends on the temperature and oxygen concentration. Up to about $UO_{2\cdot14}$, the region is best represented as $UO_{2+x} + U_4O_9$, above this ratio as $UO_{2+x} + U_4O_{9-y}$. Heating a specimen above 180°C within this region results first in an ordering of many of the oxygen atoms into the body centre of the unit cell; that is, the U_4O_9 structure is preferred. Increasing the temperature still further finally destroys the order, as shown in Fig. 9.

(3) At oxygen concentrations between $UO_{2\cdot26}$ and $UO_{2\cdot34}$ a tetragonal phase is predominant. In this structure, corresponding to the formula U_3O_7, oxygen atoms, previously interstitial in the UO_{2+x}, occupy planes perpendicular to the [001] direction of the fluorite cubic system. Indications are that this phase is stable to at least 400°C.

The study of the UO_2–U_3O_7 system by means of electrical measurements was limited to temperatures below 400°C because of changes in oxygen content at higher temperatures. The high-temperature data for large oxygen/uranium ratios of Fig. 9 were taken from PERIO's diagram.

[16] P. PERIO *Bull. Soc. chim. Fr.* 256 (1953).
[17] F. GRONVALD *J. inorg. nucl. Chem.* **1**, 357 (1955).

Indications are that the equilibria of the system are not clear cut. This is especially true of the equilibrium involving UO_2 and U_4O_9. For example, there is a large difference between the boundary of the two-phase region, $UO_2 + U_4O_9$, and the single-phase region, UO_2, given by GRONVALD and that obtained from Battelle X-ray data. This difference may possibly be attributed to the differences in anneal temperature, purity of materials (nitrogen content, etc.), and the precision to which the second phase can be detected. There is also a question of whether equilibrium was actually

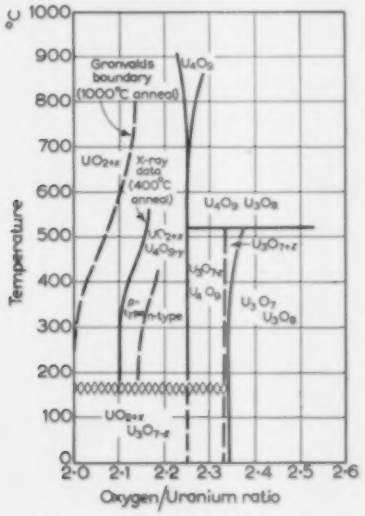

FIG. 9.—The UO_z—U_3O_7 system.

obtained during the X-ray measurements. Furthermore, the continuously increasing conductivity with increasing temperature found in the anneal-quench experiments indicates a temperature-dependent oxygen absorption for which, at low temperatures, much of the excess oxygen is not incorporated in the lattice but perhaps is precipitated at the grain boundaries. Somewhat similar results have been reported for the case of excess lead in lead telluride.[18]

From the sign and relative magnitude of the conductivity one can determine whether a phase is metal excess, metal deficit, or nearly stoicheiometric. Using this type of analysis, the discontinuity in electrical conductivity as a function of oxygen/uranium ratio (Fig. 5) becomes the broken line separating the *p*-type and *n*-type regions in the $UO_{2+x} + U_4O_{9-y}$ portion in Fig. 9. From Fig. 5 it may be seen that the electrical conductivity increases as a function of the oxygen/uranium ratio for ratios between 2·00 and 2·07, and then decreases for ratios up to 2·14. The decrease can be explained only by assuming that part of the oxygen is in a compound of a higher valence state of uranium. The second phase is confirmed by X-ray analysis. At a ratio of about 2·16, the conductivity becomes large, *n*-type, and decreases as the oxygen/uranium ratio is increased to 2·32. The large *n*-type conductivity at an oxygen/uranium ratio of about 2·16 indicates the predominance of a metal-excess phase which

[18] R. W. FRITTS and S. KARRER *Bull. Amer. phys. Soc.* 1, Ser. II, 226 (1956).

is identified as U_4O_9 by X-rays. The X-ray data also show the region to be two phase with the second phase being UO_{2+x}, the excess oxygen being indicated by a slight reduction of the lattice constant of uranium dioxide. The second phase is not in contradiction with the electrical data and may even contribute to the large values of conductivity observed. The change in slope of the *n*-type conductivity and its decrease to a very low value for an oxygen/uranium ratio of 2·32 suggest a stoicheiometric compound with an oxygen/uranium ratio slightly higher than this value. Obviously, this compound is U_3O_7, and its existence is confirmed by X-ray data.

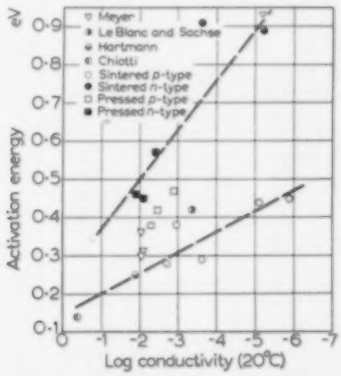

FIG. 10.—Activation energy as a function log conductivity at 20°C for various specimens of UO_2.

Electrical measurements on the quenched specimens after prolonged aging at room temperature indicate the reversibility of the phase transitions discussed above. The conductivity of all quenched specimens decreased as a function of time when allowed to age at room temperature. Although it was possible to quench in the high-temperature phases, prolonged aging resulted in the precipitation of oxygen or the appearance of U_3O_{7-z} as indicated by the phase diagram of Fig. 9.

Additional information on the phase diagram can be obtained from magnetic-susceptibility measurements. DAWSON and LISTER[19] and ARROTT and GOLDMAN[20] have determined the magnetic susceptibility of uranium oxides in the region UO_2 to U_3O_8. It is interesting to note that the anomalous magnetic susceptibility below 29°K as a function of the oxygen/uranium ratio as determined by ARROTT and GOLDMAN has a behaviour similar to the electrical conductivity at room temperature following the anneal and quench experiments. Namely, both the susceptibility and conductivity increase with increasing oxygen/uranium ratio for ratios between 2·00 and 2·10 and decrease with increasing oxygen/uranium ratio between 2·10 and 2·33. Collection of more data will be necessary, however, before definite conclusions can be drawn.

Electrical Properties of Uranium Oxides

A summary of the activation energies obtained from the slope of the curves of the logarithm of the extrinsic conductivity versus reciprocal-temperature from this investigation and from the literature is shown in Fig. 10. The *p*-type (metal deficit)

[19] J. K. DAWSON and M. J. LISTER *J. chem. Soc.* 2177 (1950).
[20] A. ARROTT and J. E. GOLDMAN *Phys. Rev.* **99**, 1641 (1955).

activation energies are about 0·37 ± 0·1 eV but apparently decrease with increasing conductivity. The lowest value of activation energy and largest room-temperature conductivity are obtained from CHIOTTI's data. The *n*-type (metal excess) activation energies are nearly double those of the *p*-type, but seem to decrease almost twice as fast with increasing conductivity. Calculations using reasonable values for the effective mass ($m^* \sim m_0$) and mobility ($\mu_p \sim 10$ cm²/V sec) of the positive current carriers give good agreement with the estimated number of acceptor levels. However, similar calculations for the *n*-type conductivity indicate that other factors must be taken into consideration. If the *n*-type material with an activation energy of about 0·9 eV contains both donors and acceptors (say, UO_{2+x} and U_3O_{7-z}), the effect is one of reducing the free carrier density. Since the saturation value (obtained at high temperatures) of free electrons is equal to the difference between the concentrations of donors and acceptors ($N_D - N_A$) and is independent of the ratio of donor to acceptor concentrations (N_D/N_A), the charge-carrier density must drop off more sharply as the temperature falls if acceptor levels are present. In fact, it has been shown[21] that when the concentration of acceptors is very much greater than the density of free electrons (from donor levels) the latter changes twice as rapidly with temperature as it would if the acceptor levels were not present. Thus, the activation energy, ΔE, of the donor levels calculated using equation (2) could be too large by a factor of 2. The large activation-energy values and their rapid decrease with increasing conductivity calculated for *n*-type material can, therefore, be explained by the above mechanism of compensation. Some of the calculations of the *p*-type activation energies may also yield values which are too high because of compensation. It is interesting to note that the value for the active oxide is low (0·28 eV) compared with most of the others, and therefore, if the above hypothesis is correct the active oxide contains negligible compensation (few or no donor or metal-excess atoms).

Although MEYER[12] reports UO_2 to be an amphoteric semiconductor no evidence for the existence of UO_{2-x} was found in the studies reported here. Measurements on a specimen with an oxygen/uranium ratio of 1·96 indicated *p*-type conductivity; therefore, the specimen was probably UO_{2+x} plus a second phase of uranium. All *n*-type conductivity observed could be attributed to the presence of U_4O_{9-y} or U_3O_{7-z}.

The electrical properties of other compounds have been found to depend on the degree of order. Of particular interest is the behaviour of the Hall coefficient of quenched specimens of Cu_3Au.[22] In the ordered state the Hall coefficient was positive, but became negative with increasing disorder. As in UO_2, the change in type of conductivity indicates that the electronic-band structure changes when ordering occurs.

The anomalous behaviour of the thermoelectric power of sintered specimens (that is, the increase of thermoelectric power with increasing conductivity) may be explained by the presence of U_3O_{7-z} at the lower temperatures and a decrease in its relative amount as the temperature is increased.

Acknowledgements—The work described here was part of an integrated investigation of the fundamental properties of uranium oxides done for the Mallinckrodt Chemical Works. The authors wish to thank J. R. BRIDGE, D. A. VAUGHAN and C. M. SCHWARTZ for the X-ray data and for helpful discussions regarding their interpretation. They also would like to thank C. HYDE for his help in carrying out the sintering operations.

[21] J. S. BLAKEMORE *Elect. Commun.* **29**, 131 (1952).
[22] A. KOMAR and S. SIDOROV *J. tech. Phys.*, Moscow **11**, 711 (1941); *J. Phys.* (*U.S.S.R.*) **4**, 552 (1941).

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THE POSSIBLE EXISTENCE OF THE CATION $POBr_2^+$ AND SOME PROPERTIES OF PHOSPHORUS OXYBROMIDE, GALLIUM TRIBROMIDE, AND THEIR IONIC 1:1 ADDITION COMPOUND

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Abstract—Phase studies show that phosphorus oxybromide reacts with gallium tribromide to form a 1 : 1 addition compound melting at 154·0°. This complex is less stable than the corresponding chloro-compound, $POCl_2^+GaCl_4^-$, but otherwise has similar properties and is considered to contain the new non-metal cation $POBr_2^+$. At 161·2° the molten compound has a density of 2·875 g ml^{-1}, a dynamic viscosity of 4·92 cP, and a specific conductivity of $1·0 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$. The density, surface tension, viscosity, and related properties of the reacting components $POBr_3$ and Ga_2Br_6 have been determined over a range of temperature and the conductivity of both liquid and solid phosphorus oxybromide has been shown to be $<4·10^{-8}\ \Omega^{-1}\ cm^{-1}$.

THE addition compound between gallium trichloride and phosphorus oxychloride is a good electrical conductor[1] and has been shown by Raman spectroscopy to contain the ions $POCl_2^+$ and $GaCl_4^-$.[2] These results prompted an investigation of the corresponding bromo-system, for, although the $GaBr_4^-$ ion is known,[3] the cation $POBr_2^+$ has not previously been reported. Indeed, even the parent donor and acceptor compounds phosphorus oxybromide and gallium tribromide have received scant attention in recent years and little is known about their physical properties. For this reason the density, surface tension, and viscosity of these compounds were determined over a range of temperature and the results used to calculate the activation energy of viscous flow, parachor, surface free energy, and related properties. The electrical conductivity of molten gallium tribromide is known to be small[4] and phosphorus oxybromide was found to be a non-conductor. It was originally intended to compare these properties with those of the 1 : 1 addition compound, $GaBr_3 \cdot POBr_3$, which had been found from phase studies, but the complex underwent some decomposition above the melting point and this restricted the amount of information obtainable from it. However, sufficient data were obtained to show that the compound was appreciably ionized in the molten state.

EXPERIMENTAL

Phosphorus oxybromide was prepared by adding the calculated amount of bromine to phosphorus tribromide and then heating the phosphorus pentabromide so formed with a slight excess of phosphorus pentoxide for several days at 70°.[5] The product was distilled from the all-glass preparation apparatus at atmospheric

[1] N. N. GREENWOOD and K. WADE *J. chem. Soc.* 1516 (1957).
[2] L. A. WOODWARD *Proc. Chem. Soc. Meetings, Cambridge* 1957. To be published.
[3] L. A. WOODWARD and A. A. NORD *J. chem. Soc.* 2655 (1955).
[4] N. N. GREENWOOD and I. J. WORRALL *J. inorg. nucl. Chem.* **3**, 357 (1957).
[5] E. BERGER *Bull. Soc. Chim.* **3** (4) 721 (1908); *Inorganic Syntheses* Vol. II, p. 151. McGraw-Hill, New York (1946).

pressure and freed from remaining traces of phosphorus tribromide and hydrolysis products by vacuum fractionation at 80°. Final purification was effected by repeated fractional freezing of the molten compound in an evacuated vessel until cryoscopic homogeneity was attained. The m.p. was 56·4°, as compared with the best literature values of 55°–56°.[5,6]

Gallium tribromide (m.p. 122·5°) was prepared and purified as previously outlined.[4] The measurement of density, surface tension, and viscosity under vacuum conditions has also been described[7] as have the circuit and cells used to determine the electrical conductivity.[1,4]

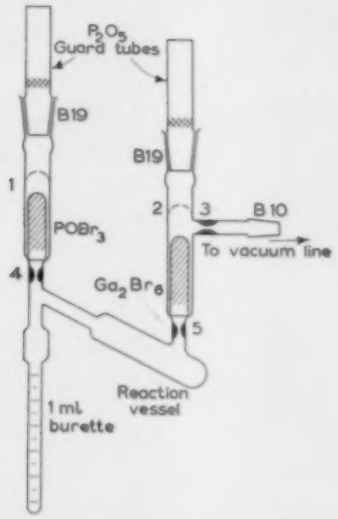

FIG. 1.—Preparation of mixtures of known composition for phase diagram.

The preparation under anhydrous conditions of mixtures of known composition for melting-point determinations presented some difficulty, as the involatility of the compounds at room temperature precluded manipulation by conventional vacuum-line techniques. The apparatus used is shown in Fig. 1. A sealed tube of phosphorus oxybromide was opened and placed in the left-hand limb, which was then sealed at position 1. A similar tube containing gallium tribromide was weighed, broken open cleanly, and then sealed into the right-hand limb at point 2, after which the apparatus was evacuated and sealed off at point 3. The phosphorus oxybromide was melted into the burette tube, the gallium tribromide sublimed into the reaction vessel, and the unwanted sections of the apparatus drawn off at points 4 and 5. The weight of gallium tribromide used was found by difference and in two runs was 0·1824 g and 1·1763 g. Successive amounts of phosphorus oxybromide were poured into the reaction vessel from the Grade A 1 ml burette which was placed in a thermostated oil-bath at 62·3°, the weight added being calculated from the density of the ligand and the heights of the meniscus as measured on a cathetometer reading to 0·01 mm (0·14 mg). After each addition the contents of the reaction vessel were melted to

[6] A. BESSON *C. R. Acad. Sci., Paris* **124**, 763 (1897); J. H. SECRIST and L. O. BROCKWAY *J. Amer. chem. Soc.* **66**, 1941 (1944); W. GERRARD, A. NECHVATAL and P. L. WYVIL *Chem. & Ind. (Rev.)* 437 (1947).
[7] N. N. GREENWOOD and K. WADE *J. inorg. nucl. Chem.* **3**, 349 (1957).

obtain a homogeneous mixture, after which the melting point of the resolidified mass was determined by heating the vessel very slowly and observing the temperature of disappearance of the solid phase on a calibrated thermometer.

The 1 : 1 addition compound $GaBr_3 \cdot POBr_3$ was prepared by the same method, using a 5 ml burette. After purification by fractional freezing the m.p. was 154·0°. Above this temperature the complex became grey and opaque, but colourless crystals could be reobtained by allowing the liquid to solidify. Under these conditions it was not possible to measure physical properties over a range of temperatures except for the density, which appeared to be insensitive to the (partially reversible) decomposition occasioned by fusion. The m.p. itself also appeared relatively insensitive to the presence of the small amounts of decomposition products.

RESULTS

Phosphorus oxybromide. The density of phosphorus oxybromide was determined on a sample which had been vacuum-distilled into a fractional freezing unit and then transferred without breaking the vacuum into a double-capillary dilatometer. The results, which have been corrected for bouyancy and for thermal expansion of the glass, are given in Table 1 and may be represented by the equation:

$$d_4^t = 2{\cdot}8335 - 2{\cdot}487 \times 10^{-3}(t - 55)$$

TABLE 1.—DENSITY OF LIQUID PHOSPHORUS OXYBROMIDE

$t°$	62·3	65·5	69·6	75·6	82·0	85·2	90·4	95·6
d_4^t	2·8161	2·8068	2·8011	2·7813	2·7664	2·7576	2·7453	2·7308
$t°$	99·8	104·4	110·2	114·6	120·2	125·0	130·0	
d_4^t	2·7213	2·7096	2·6968	2·6858	2·6713	2·6594	2·6474	

These figures appear to be the first data on the density of liquid phosphorus oxybromide. RITTER[8] found the density of the solid to be $d_4^{20} = 2{\cdot}822$ on a sample which melted some 11° below the present m.p.; a value of $d_4^{20} = 3{\cdot}23$ may be obtained by extrapolation of data[9] obtained between −183° and −21° and, if an allowance of about 10 per cent is made for expansion on fusion, this latter value is seen to be reasonably consistent with the present figures.

The surface tension of phosphorus oxybromide was estimated in a separate run between 100° and the m.p. by measuring the lengths of liquid in the two capillaries of the dilatometer and making an appropriate meniscus correction. A least-squares treatment of the 11 values lead to the equation:

$$\gamma = 41{\cdot}2 - 0{\cdot}167(t - 55)$$

This represents the surface tension with a mean deviation of 1·7 dyne cm^{-1}. The corresponding surface free energy ($\omega = \gamma V_M^{2/3}$, where V_M is the molar volume) is given by

$$\omega = 895 - 3{\cdot}22(t - 55)$$

[8] H. RITTER *Liebigs Ann.* **95**, 208 (1855).
[9] W. BILTZ, A. SAPPER and E. WÜNNENBERG *Z. anorg. Chem.* **203**, 277 (1932).

in which the Eötvös constant k has the rather large value of 3·22. The parachor, ($[P] = V_M\gamma^{1/4}$), calculated from the 11 independent values of surface tension, had a mean value of 255·3 ± 3·4, compared with a value of 254·3 calculated by McGowan's method.[10]

The viscosity of phosphorus oxybromide was measured in a sealed, all-glass, capillary viscometer having an overflow wier.[11] Outflow times varied between 175 and 275 sec. The results are summarized in Table 2, which lists the kinematic viscosity (ν cS) the dynamic viscosity (η cP $= \nu d_4^t$) and the fluidity (ϕ cP^{-1}). The reproducibility of the data and the stability of the compound are shown by the fact that the viscosities at the first three temperatures in Table 2 were measured at the conclusion of the run when the thermostat had cooled down from 93°; graphically they are indistinguishable from the rest of the data.

Table 2.—Viscosity and fluidity of phosphorus oxybromide

$t°$	ν (cS)	η (cP)	ϕ (cP^{-1})	$t°$	ν (cS)	η (cP)	ϕ (cP^{-1})
54·5	0·9627	2·729	0·3663	75·4	0·7312	2·035	0·4914
56·0	0·9459	2·679	0·3734	77·3	0·7154	1·987	0·5031
58·0	0·9181	2·594	0·3854	79·9	0·6930	1·921	0·5206
60·0	0·8957	2·527	0·3957	82·5$_5$	0·6737	1·863	0·5368
62·3	0·8690	2·446	0·4087	85·2$_5$	0·6561	1·810	0·5526
65·1	0·8378	2·353	0·4250	87·0	0·6442	1·774	0·5638
66·6	0·8177	2·294	0·4359	89·1	0·6356	1·734	0·5770
69·7	0·7863	2·199	0·4546	91·1	0·6169	1·693	0·5907
72·0	0·7641	2·132	0·4690	93·1$_5$	0·6043	1·655	0·6043
73·2	0·7534	2·101	0·4761				

A plot of log η against $1/T°$K is slightly curved, the activation energy of viscous flow (E_η) decreasing from 3·21 kcal mole^{-1} at the m.p. to 2·85 kcal mole^{-1} at 90°. It may be noted that the latent heat of vaporization of phosphorus oxybromide is 10·9 kcal mole^{-1},[12] so that the ratio $\Delta H_{vap}/E_\eta$ is in the range 3·4–3·8, in agreement with the theory of absolute reaction rates.

The electrical conductivity of a sample of phosphorus oxybromide which had been distilled under vacuum into a cell was too small to be measured with the apparatus used. This places an upper limit of $4 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ on the conductivity. The solid was also non-conducting.

Gallium tribromide. The density of molten gallium tribromide (Ga_2Br_6) is presented in Table 3. It corresponds to the equation

$$d_4^t = 3{\cdot}1199 - 2{\cdot}47 \times 10^{-3}(t - 120)$$

which may be compared with the equation of Klemm and Tilk[13] based on values between 139° and 230°.

$$d_4^t = 3{\cdot}15_3 - 2{\cdot}9_5 \times 10^{-3}(t - 120)$$

[10] J. C. McGowan *Rec. Trav. chim. Pays-Bas* **75**, 193 (1956).
[11] N. N. Greenwood and K. Wade *J. sci. Instrum.* **34**, 288 (1957).
[12] M. Van Driel *Rec. Trav. chim. Pays-Bas* **61**, 748 (1942).
[13] W. Klemm and W. Tilk *Z. anorg. Chem.* **207**, 161 (1932).

The two other published values [14] are also higher than the present values but are not concordant: $d_4^{120} = 3{\cdot}123$, $3{\cdot}138$.

TABLE 3.—DENSITY OF LIQUID GALLIUM TRIBROMIDE

$t°$	117·8	119·2	120·3	121·3	122·4	123·4	124·4	125·7
d_4^t	3·1256	3·1213	3·1189	3·1173	3·1138	3·1107	3·1090	3·1048
$t°$	127·7	129·0	130·1	132·2	133·3	134·8	135·9	
d_4^t	3·1004	3·0976	3·0941	3·0897	3·0869	3·0837	3·0806	

The surface tension of gallium tribromide in the same temperature range may be represented to ± 2 dyne cm^{-1} by the equation

$$\gamma = 35{\cdot}5 - 0{\cdot}15(t - 120)$$

This leads to a surface free energy equation

$$\omega = 1200 - 4{\cdot}5(t - 120)$$

The lack of precision in the surface tension measurements is due to the fact that capillary diameters which are desirable for density measurements are not the optimum diameters for surface tension determinations. Nevertheless the results give a reasonable indication of the magnitude of the surface tension. The mean of ten concordant parachors calculated from individual values of the surface tension is $[P] = 482{\cdot}0 \pm 2{\cdot}5$. The mean of all 15 values is $482{\cdot}7 \pm 5{\cdot}8$ and the calculated value for the bridged dimer Ga_2Br_6 is 482·0.

The viscosity of gallium tribromide was measured over a period of three days to check reproducibility and stability. Times of outflow were similar to those observed for phosphorus oxybromide and varied between 225 and 275 sec. The results are collected in Table 4 which also indicates the sequence of measurements. The activation energy of viscous flow decreases slowly from 3·94 kcal mole^{-1} at the m.p. to

TABLE 4.—VISCOSITY OF GALLIUM TRIBROMIDE

No.	$t°$	ν (cS)	η (cP)	No.	$t°$	ν (cS)	η (cP)
17	117·6	0·9766	3·052	11	128·0	0·8639	2·678
16	118·8	0·9623	3·004	10	129·0	0·8535	2·644
15	119·8	0·9502	2·965	12	130·0	0·8435	2·611
14	121·0	0·9363	2·919	4	131·3	0·8335	2·577
13	122·0	0·9267	2·887	5	132·5	0·8228	2·542
1	123·4	0·9096	2·830	6	133·6	0·8117	2·505
19	124·2	0·9014	2·803	7	135·0	0·7999	2·465
2	125·1	0·8935	2·776	8	136·3	0·7888	2·429
18	126·1	0·8817	2·738	9	137·4	0·7800	2·400
3	127·1	0·8732	2·709				

[14] W. C. JOHNSON and J. B. PARSONS *J. phys. Chem.* **34**, 1210 (1930).

3·70 kcal mole^{-1} at 135°. This is less than the latent heat of evaporation, 14·3 kcal mole^{-1} [15] by a factor of 3·6–3·8 as expected.

Gallium tribromide–phosphorus oxybromide. The existence of an addition compound $GaBr_3 \cdot POBr_3$ was established by the melting-point diagram shown in Fig. 2 which was obtained by adding successive amounts of phosphorus oxybromide to

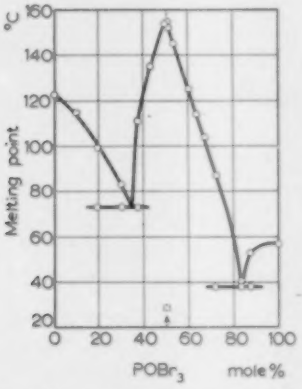

FIG. 2.—Phase diagram of the system gallium tribromide–phosphorus oxybromide.

known weights of gallium tribromide. The maximum m.p. is 155° and occurs at the 1 : 1 ratio; this m.p. is slightly above that of the purified complex (154·0°) since, in phase studies, the mixture is heated slowly until the last disappearance of the solid

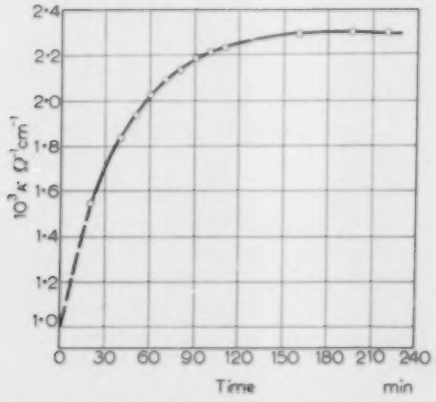

FIG. 3.—Variation of conductivity with time after fusion.

phase, whereas the m.p. quoted for the pure compound was the temperature of first appearance of liquid when individual crystals were heated.

The density of the complex over a range of temperature may be represented by the equation

$$d_4^t = 2{\cdot}8855 - 1{\cdot}62 \times 10^{-3}(t - 155)$$

[15] W. FISCHER and O. JUBERMANN *Z. anorg. Chem.* **227**, 227 (1936).

Because of the tendency for the complex to undergo some decomposition above the m.p., the true surface tension could not be measured, but the complex gave a reproducible value of the viscosity when measured at 161·2°:

$$\nu = 1{\cdot}712 \text{ cS}; \qquad \eta = 4{\cdot}921 \text{ cP}.$$

The conductivity of the complex increased with time at 161·2°, but reached a steady value of $2{\cdot}302\ \Omega^{-1}\ \text{cm}^{-1}$ after 3 hr. This variation is plotted in Fig. 3. Zero time is the time at which melting began, and the first reading, taken 20 min later when thermal equilibrium had been established at 161·2°, was $1{\cdot}540 \times 10^{-3}$. Extrapolation to zero time gives a conductivity of about $1{\cdot}0 \times 10^{-3}$.

DISCUSSION

Before the structure of the addition compound $GaBr_3{\cdot}POBr_3$, is discussed two points which arise from the properties of the components will be considered. The first concerns the parachor which can now be calculated accurately by means of the modified table of atomic parachors due to MCGOWAN.[10] In an earlier paper[7] GREENWOOD and WADE pointed out that no satisfactory method for reproducing the parachor of compounds of gallium had been devised. Values calculated from MCGOWAN's original table,[16] using an extrapolated value for gallium itself, gave 418·0 for gallium trichloride instead of the observed value of 392·0; with the modified table the calculated value becomes 392·6, in excellent agreement with the experimental value. For gallium tribromide the experimental and calculated values are identical, 482·0. The parachor has an unenviable history in structural chemistry and it would be rash to claim that the present results imply further evidence for the already well-established bridged dimer structure of the gallium halides (the calculated values for $2GaCl_3$ and $2GaBr_3$ being 429·8 and 519·2 respectively). Nevertheless, it is important to establish that at least one scheme can be used for computing the parachor of compounds containing gallium, since this serves as an admirable check on the experimental values of the surface tension.

The second property for discussion is the viscosity. Complex formation is accompanied by a considerable increase in viscosity of the system, the viscosity of the complex at its m.p. being approximately twice those of the donor and acceptor compounds at their melting points; the disparity would be even greater if the comparisons were made all at the same temperature. It has also been shown that the activation energies of viscous flow for phosphorus oxybromide and gallium tribromide have values agreeing with those expected from the known heats of evaporation of these compounds. Of more interest is an alternative representation of viscosity by an equation involving the fluidity ($\phi = \eta^{-1}$) and the specific volume ($v = d^{-1}$):

$$v = b + B\phi,$$

where b and B are constants. Linear plots were obtained in this way for both the parent compounds, values for Batschinski's constant B being obtained from the slope. For phosphorus oxybromide $B = 5{\cdot}13 \times 10^{-2}$ ml cP g^{-1}; for gallium tribromide $B = 5{\cdot}60 \times 10^{-2}$ ml cP g^{-1}. The magnitude of B is often taken as being roughly proportional to the size of the flow unit in a liquid. It is therefore interesting

[16] J. C. MCGOWAN *Chem. & Ind. (Rev.)* 495 (1952).

to observe that the values for the two bromides are both *less* than those for the corresponding chlorides ($POCl_3$, $6{\cdot}45 \times 10^{-2}$, Ga_2Cl_6, $5{\cdot}75 \times 10^{-2}$)[1] despite the fact that their molar volumes are *greater*. Other instances of this type of reversal may be found in the literature, for example the trichlorides and tribromides of phosphorus and arsenic, and the tetrachlorides and tetrabromides of silicon and tin.[17] It may be argued that the size of flow units on a molecular scale is not necessarily proportional to the bulk molar volume of a liquid and that chlorides might be more likely to associate or interact than the bromides, but such interaction seems unlikely, especially in those halides which are highly symmetrical such as the gallium trihalides and the tetrahalides of silicon and tin.

The electrical conductivity of phosphorus oxybromide is $<4.10^{-8}\,\Omega^{-1}\,cm^{-1}$ and that of liquid gallium tribromide is $7.10^{-6}\,\Omega^{-1}\,cm^{-1}$ at its melting point. By contrast, the complex $GaBr_3{\cdot}POBr_3$ has a conductivity of $1{\cdot}0 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ when first melted at 161·2°, and this value increases during 3 hr to a constant value of $2{\cdot}3 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$. It is unlikely that the conduction is due entirely to traces of decomposition products, firstly because the compound shows appreciable conductivity immediately on melting (although time is required for complete fusion and the attainment of thermal equilibrium), and secondly because the conductivity rapidly reaches an equilibrium value of the same order of magnitude as the initial conductivity. If one assumes that ionic mobility is viscosity-controlled, as it normally is in such self-ionizing complexes, then the ionic concentration required to give the observed conductivity is about 0·1 M; such a concentration of impurity would certainly lower the m.p. of the compound, but this is not observed.

In fact, there is no reason to suppose that the conductivity is not due predominantly to self-ionic dissociation of the molten complex. The initial conductivity of $1{\cdot}0 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ corresponds to a molar conductivity, μ, of $0{\cdot}21\,\Omega^{-1}\,cm^2$ and a reduced conductivity, $\mu\eta$, of $1{\cdot}0\,\Omega^{-1}\,cm^2$ cP. These values are strikingly similar to those of the corresponding chloro-complex $GaCl_3{\cdot}POCl_3$ at its m.p. of 118·5°: $\kappa = 1{\cdot}26 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$, $\mu = 0{\cdot}227\,\Omega^{-1}\,cm^2$, and $\mu\eta = 0{\cdot}442\,\Omega^{-1}\,cm^2$ cP.[1] It seems reasonable to suppose, therefore, that the structures of the two complexes are analogous. The Raman spectrum of molten gallium trichloride-phosphorus oxychloride has been interpreted exclusively in terms of the ions $POCl_2^+$ and $GaCl_4^-$[2] and it is suggested that the present complex should be formulated as $POBr_2^+GaBr_4^-$. An unequivocal demonstration of the presence of the new cation $POBr_2^+$ by Raman spectroscopy may prove difficult because of the opacity which develops on fusion, but it is hoped to prepare analogous complexes, for example with aluminium or indium tribromides, in the hope that these may prove more amenable to structural investigation by physical techniques.

Acknowledgements—The authors thank the Chemical Society for a Grant from the Research Fund and acknowledge the award of a University of Nottingham Research Scholarship to I. J. W.

[17] G. P. Luchinski *J. gen Chem., Moscow* **7**, 2116 (1937).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 42 to 51. Pergamon Press Ltd., London

PROPERTIES OF A LIQUID METAL CHELATE ALUMINIUM *ISO*VALERYLACETONATE

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Abstract—The aluminium chelate derived from *iso*valerylacetone has been found to be a liquid at room temperature. A number of physical properties of the substance, including vapour-pressure, density, viscosity, and dielectric constant, have been studied over a range of temperatures. Based on the vapour-pressure and viscosity data, the liquid appears to be highly associated. Dielectric constant measurements indicate no permanent dipole moment, but do indicate a high atomic polarization for the substance.

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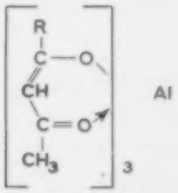
DESPITE the interest in metal chelate compounds, little is known of the properties of these substances in the liquid state. This is probably due, at least in part, to the fact that most such compounds are either infusible or melt at inconveniently high temperatures. In the present work it was found that the aluminium chelate derived



from *iso*valerylacetone (I, R = $(CH_3)_2CHCH_2$) was liquid at temperatures considerably below room temperature. The present paper describes the preparation of this compound and presents data on a number of its physical properties, determined over a range of temperatures.

EXPERIMENTAL

The chelate was prepared by the interaction of aluminium *iso*propoxide with *iso*valerylacetone.

$$(iso\text{-}C_3H_7O\text{—})_3Al + 3(CH_3)_2CH\text{—}CH_2\text{—}\overset{OH}{\overset{|}{C}}\text{=}CH\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3$$
$$\longrightarrow I(R = (CH_3)_2CH\text{—}CH_2) + 3\ iso\text{-}C_3H_7OH$$

Thirty-four grams (0·167 mole) of aluminium *iso*propoxide were added, in small portions, to 71·1 g (0·5) mole *iso*valerylacetone (Midcontinent Chemical Company). Heat was evolved after each addition. After the reaction had subsided, the flask was heated with a heating mantle for an hour, gradually raising the temperature to 150°C, and the formed *iso*propyl alcohol collected as it distilled out of the reaction mixture (obtained 37·5 ml, theoretical 38·0 ml). The product remaining in the flask was vacuum distilled. After a small fore fraction, 49·0 g was collected (b.p. 170–172°C at 1 mm). Yield = 65 per cent. The chelate was also prepared, using twice the above

quantities with a slightly lower yield. The material taken for the physical measurements was fractionated under reduced pressure, reiecting large fore and after fractions (Found: C, 63·86; H, 8·21; Al, 6·05. Calc. for $(C_8H_{13}O_2)_3Al$: C, 63·98; H, 8·72; Al, 5·98). (M.W.: Found 405, 444 (cryoscopically in dioxane). Calc. 450·5). n_D^{25} 1·5107.

The product was a light yellow, viscous liquid. All attempts to induce crystallization failed. The liquid formed a glass when cooled with dry ice and acetone. The chelate remained liquid for many months when stored at room temperature.

Vapour pressure

Vapour pressure was studied as a function of temperature, using an isoteniscope and furnace designed by Dr. ALAN DOBRY of these laboratories. Temperature was measured with a chromel–alumel thermocouple touching the isoteniscope. Pressure was measured with a closed-end mercury manometer.

It was observed that pressure readings increased slowly with time, especially at the higher temperatures, indicating some decomposition of the chelate. The procedure was therefore adopted of boiling out the volatile decomposition products at each temperature by lowering the external pressure below the vapour-pressure of the liquid. The liquid levels in the manometer portion of the isoteniscope were then balanced and readings taken rapidly. Above 300°C decomposition occurred too rapidly for useful data to be obtained.

Density

Density was measured with a 25 ml. Weld type pycnometer. A constant-temperature water-bath regulating to ±0·01°C was employed for the temperature range 30–55°C. In the range 80–100°C a large oil-bath regulating to ±0·1°C was employed. A small dibutyl phthalate bath regulating to ±0·2°C was used above 100°C. The pycnometer was calibrated at 30°C with distilled water. Densities were calculated in the usual manner, taking into account the expansion of the glass and buoyancy corrections.

Viscosity

Viscosity was measured with CANNON–FENSKE viscometers[1] calibrated by the manufacturer and having efflux times greater than 200 sec. It was necessary to use four different viscometers to cover the range studied. Efflux times were measured to ±0·2 sec with a stopwatch or electric timer. Viscosities were run concurrently with densities in the same constant-temperature baths. Viscosities were calculated from the efflux times and densities in the usual manner. No kinetic energy corrections were made. Two determinations were made at 40°C, using viscometers differing in efflux times by a factor of 20. Calculated viscosities agreed within 1 per cent, indicating that the flow is Newtonian at this temperature.

Dielectric measurements

These measurements were made with a General Radio Capacitance Bridge, Type 716-ASl, and a 25 ml Balsbaugh dielectric cell, over a range of frequencies and temperatures. The cell was mounted in a constant temperature oven. The

[1] M. R. CANNON and M. R. FENSKE *Ind. Eng. Chem.* (*Anal.*) **10**, 298 (1938).

dielectric constant results were combined with interpolated density values to calculate molar polarization by means of equation (2).

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \tag{2}$$

where M is the calculated molecular weight for the chelate (450·5).

The refractive index of the chelate at 25°C was determined with a Bausch and Lomb "Abbe-56" refractometer. The molar refraction was calculated from equation (3).

$$MR = \frac{(n_D)^2 - 1}{(n_D)^2 + 2} \cdot \frac{M}{d} \tag{3}$$

Ultra-violet absorption spectra

The ultra-violet absorption spectra of the aluminium chelates of *iso*valerylacetone and of acetylacetone were determined with a Beckman DU spectrophotometer equipped with photomultiplier attachment. Solutions ($1{\cdot}55 \times 10^{-5}$ M) of the chelates in absolute ethanol were prepared by volumetric dilution of 0·01 M solutions. All solutions were prepared immediately before measurement.

Molar extinction coefficients were calculated from equation (4)

$$\epsilon = \frac{OD}{cl} \tag{4}$$

where OD is the measured optical density, c is the molar concentration and l = length of optical path (1 cm for the quartz cells employed).

Coefficient of friction

Incidental to the present work, the coefficient of friction characteristic of aluminium *iso*valerylacetonate on steel surfaces was determined at room temperature (26°C), using the pendulum apparatus described by MAHNCKE.[2] The compound was found to have fair, but not outstanding, lubricating properties. Coefficient of friction = 0·133.

RESULTS AND DISCUSSION

The fact that aluminium *iso*valerylacetonate is a liquid is striking when one considers that the closely related aluminium acetylacetonate (I, R = CH_3) melts at 192°C. This difference may be related to the fact that acetylacetone is a symmetrical donor molecule, while *iso*valerylacetone is unsymmetrical. Aluminium acetylacetonate may exist as two optically active forms[3] (although these have not been demonstrated), but no geometric isomerism is possible. On the other hand, *cis–trans* isomerism is possible for aluminium *iso*valerylacetonate.[4] The latter compound can, at least in principle, exist as two pairs of optical enantiomorphs. If both *cis* and *trans* forms do exist, they may well depress each other's melting points to give a low melting mixture. It should be borne in mind, however, that *cis–trans* isomerism has not been

[2] H. E. MAHNCKE *Lubric. Engng.* **12**, 85 (1956).
[3] A. E. MARTELL and M. CALVIN *Chemistry of the Metal Chelate Compounds* p. 296. Prentice Hall, New York (1952).
[4] A. E. MARTELL and M. CALVIN *Chemistry of the Metal Chelate Compounds* p. 297. Prentice Hall New York (1952).

shown to exist for aluminium chelates of β-diketones. The possibility exists that one of the two forms may be favoured energetically to the complete exclusion of the other.

It is interesting to note that aluminium propionylacetonate (I, R = CH_2CH_3),

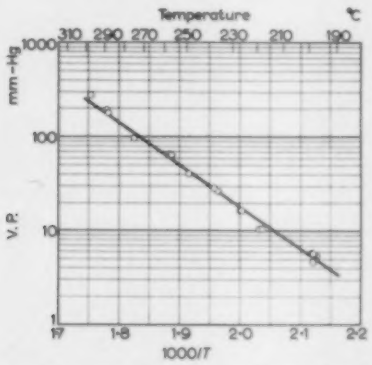


FIG. 1.—Vapour pressure as a function of reciprocal absolute temperature for aluminium *iso*valerylacetonate.

which is also derived from an unsymmetrical donor, melts at 35°C, very much lower than the melting point of aluminium acetylacetonate.

Vapour pressure

Vapour-pressure results for aluminium *iso*valerylacetonate are presented graphically in Fig. 1. The logarithm of the vapour-pressure is linear with reciprocal absolute temperature and obeys equation (5).

$$\log p = 10{\cdot}15 - \frac{4{\cdot}44 \times 10^3}{T} \tag{5}$$

From this equation the boiling point at 760 mm is calculated to be 338°C. The

TABLE 1.—HEATS AND ENTROPIES OF VAPORIZATION FOR ALUMINIUM ALKOXIDES

Alkoxide	ΔH_{vap} (kcal/mole)	$\Delta H_{vap}/T_{760}$
$Al(OC_2H_5)_3$	23·9	41·7
$Al(n\text{-}OC_3H_7)_3$	27·5	44·4
$Al(iso\text{-}OC_3H_7)_3$	19·4	38·9
$Al(n\text{-}OC_4H_9)_3$	29·9	44·8
$Al(sec\text{-}OC_4H_9)_3$	21·6	38·4

latent heat of vaporization (ΔH_{vap}) for aluminium *iso*valerylacetonate is calculated from the slope of the line in Fig. 1 to be 20·3 kcal/mole. The entropy of vaporization at the normal boiling point (Trouton's constant = $\Delta H_{vap}/T_{760}$) is found to be 33·3 e.u. Trouton's constant is stated to be nearly the same for all "normal" liquids and equal

to about 21 e.u.[5] The higher value found in the present case is evidence that aluminium *iso*valerylacetonate is associated at the normal boiling point.

There are few vapour-pressure data for metallic chelates of β-diketones with which to compare the above results. That a high entropy of vaporization may be characteristic of other aluminium-organic compounds, however, is shown by the data of MEHROTRA[6] for aluminium alkoxides. In Table 1 are shown MEHROTRA's values for ΔH_{vap} and the corresponding entropies of vaporization, recalculated from MEHROTRA's data to the normal boiling point. The latter entropy values are also much larger than the usual value of 21 e.u.

Density and molar volume

The density results for aluminium *iso*valerylacetonate are listed in Table 2.

TABLE 2.—DENSITY AND VISCOSITY OF THE ALUMINIUM CHELATE OF *iso*VALERYLACETONE AS A FUNCTION OF TEMPERATURE

t (°C)	d_4^t	η (cP)
20·0	—	61900
25·0	—	21500
30·0	1·0252	8420
40·0	1·0164	1750
50·0	1·0075	519
55·0	1·0029	310
80·0	0·9809	44·9
100·0	0·9634	16·2
125·5	0·9407	6·45
148·5	0·9198	3·54
176·9	0·8936	1·96

Specific volumes ($v_t = 1/d_4^t$), calculated from the density data, obey equation (6)

$$v_t = 0{\cdot}9509 + 7{\cdot}92 \times 10^{-4}t + 8{\cdot}48 \times 10^{-7}t^2 \qquad (6)$$

within experimental error.

It is interesting to compare the results obtained with the limited density data available for aluminium chelates of other β-diketones. Molar volumes (V_t = molecular weight $\times$ v_t) were calculated at 150°C, for aluminium *iso*valerylacetonate from the present data and for aluminium acetylacetonate and aluminium propionylacetonate from literature data.[7,8] If it can be assumed that the total effective volume for the three ring systems (formula I) is the same in each case, then V_{150} should be a function of the volume of the groups attached to the chelate rings, (CH_3 and R in I). In Fig. 2, V_{150} is plotted against three times the sum of the volumes of CH_3 and R, the latter two quantities calculated from the atomic volumes listed by KOPP.[9] The three points fall well on a straight line. The slope of the line is

[5] S. GLASSTONE *Text Book of Physical Chemistry* p. 450. D. Van Nostrand, New York (1940).
[6] R. C. MEHROTRA *J. Indian chem. Soc.* **30**, 585 (1953).
[7] R. A. ROBINSON and D. A. PEAK *J. phys. Chem.* **39**, 1125 (1935).
[8] S. SUGDEN *J. chem. Soc.* 316 (1929).
[9] J. A. LEERMAKERS and A. WEISSBERGER *Organic Chemistry, An Advanced Treatise* (2nd Ed. Edited by H. GILMAN) p. 1743. John Wiley, New York (1943).

somewhat less than unity. This is a consequence of the fact that KOPP's values are strictly applicable only at the normal boiling points of the compounds.

Viscosity

The viscosity results for aluminium *iso*valerylacetonate are listed in Table 2.

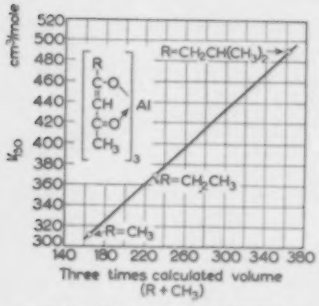


FIG. 2.—Variation of molecular volumes of aluminium β-diketone chelates with the calculated volumes of the groups attached to the chelate rings.

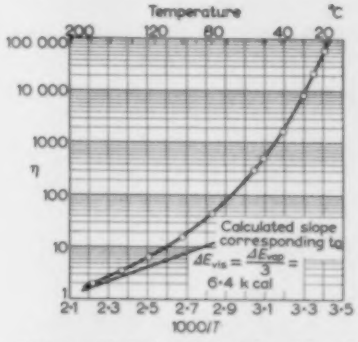


FIG. 3.—Variation of viscosity with reciprocal of absolute temperature for aluminium *iso*valerylacetonate.

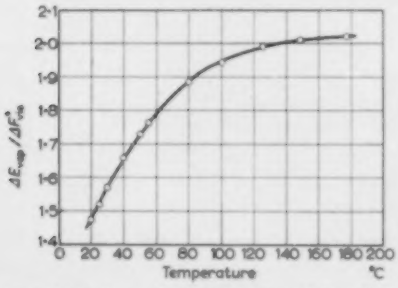


FIG. 4.—Variation of the quantity ($\Delta E_{vap}/\Delta F_{vis}$) with temperature for aluminium *iso*valerylacetonate.

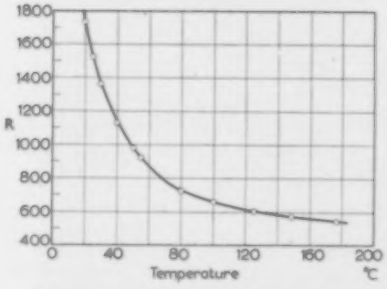


FIG. 5.—Variation of rheochor with temperature for aluminium *iso*valerylacetonate.

The viscosity is markedly dependent on temperature, changing through five orders of magnitude over the temperature range studied.

A plot of log η against the reciprocal of absolute temperature in general gives a straight line for unassociated liquids, the slope of which is proportional to the energy of activation for viscous flow for the substance.[10] A plot of this type for aluminium *iso*valerylacetonate is shown in Fig. 3. The fact that the curve is not linear indicates that the liquid is associated;[11] and the magnitude of the departure from linearity suggests a high degree of association, particularly at the lower temperatures.

EYRING *et al.*[10] have shown that for many liquids composed of spherical molecules the energy of activation for viscous flow (E_{vis}) is about one-third of the energy of vaporization (ΔE_{vap}), the latter quantity being related to ΔH_{vap} by equation (7).

$$\Delta E_{vap} = \Delta H_{vap} - RT \qquad (7)$$

[10] S. GLASSTONE, K. J. LAIDLER, and H. EYRING *The Theory of Rate Processes* p. 494. McGraw-Hill, New York (1941).

The straight line in Fig. 3 has been drawn with a slope corresponding to $\Delta E_{vap}/3$, the latter calculated from ΔH_{vap} for aluminium *iso*valerylacetonate and $T = 611°K$. The curve in Fig. 3 appears to approach this slope with increasing temperature. The slope at the lower temperatures is very much larger than that corresponding to $\Delta E_{vap}/3$. For example, at 20°C the slope corresponds to an energy of activation for viscous flow of about 38 kcal/mole.

EYRING has also shown that for many liquids the ratio of ΔE_{vap} to the standard free energy for viscous flow ($\Delta F^{\ddagger}_{vis}$) is approximately constant.[12]

$$\frac{\Delta E_{vap}}{\Delta F^{\ddagger}_{vis}} = 2{\cdot}45 \tag{8}$$

$\Delta F^{\ddagger}_{vis}$ is given by equation (9)

$$\Delta F^{\ddagger}_{vis} = RT \ln \frac{V\eta}{hN} \tag{9}$$

where V is the molar volume, h is Planck's constant and N is Avogadro's number.

In the present case $\Delta E_{vap}/\Delta F^{\ddagger}_{vis}$ was found to vary with temperature. A plot of $\Delta E_{vap}/\Delta F^{\ddagger}_{vis}$ vs. temperature is shown in Fig. 4. The curve appears to approach a limit somewhat lower than 2·45, as the temperature is increased.

FRIEND[13] has proposed a function involving viscosity and density which is obeyed by many liquids.[14]

$$R = M\eta^{1/8}/(d + 2d') \tag{10}$$

Where M is molecular weight, d is the density of the liquid, and d' the density of the vapour (assumed negligible in the present case). R, the rheochor, is a constant characteristic of the substance. For unassociated liquids, R shows only second-order dependence on temperature. In Fig. 5, rheochor values calculated from the data in Table 2 for aluminium *iso*valerylacetonate are plotted as a function of temperature. It is seen that the rheochor values decrease markedly with temperature, but appear to approach a limit at the higher temperatures.

The viscosity results together with the vapour pressure data suggest that aluminium *iso*valerylacetonate is a highly associated liquid. The association appears to decrease with increasing temperature, but is apparently still appreciable at the normal boiling point.

The reason for association in liquid aluminium *iso*valerylacetonate is not obvious. According to the commonly accepted structure for aluminium β-diketone chelates of this type (I), all the reactive groups are bonded to the aluminium, which is co-ordinatively saturated. One would expect only weak forces between such molecules, since the outer surfaces of the molecules are essentially hydrocarbon in nature.

The molecular weight of aluminium *iso*valerylacetonate was determined cryoscopically in 1,4-dioxane. At the concentrations employed (ca. 0·1 M) there appears to be

[11] S. GLASSTONE, K. J. LAIDLER, and H. EYRING *The Theory of Rate Processes* p. 505. McGraw-Hill, New York (1941).
[12] S. GLASSTONE, K. J. LAIDLER, and H. EYRING *The Theory of Rate Processes* p. 492. McGraw-Hill, New York (1941).
[13] J. N. FRIEND and W. HARGREAVES *Phil. Mag.* **34**, 643 (1943).
[14] F. E. MCGOURY and H. MARK *Physical Methods of Organic Chemistry* (2nd Ed. Edited by A. WEISSBERGER) Part I, p. 346. Interscience, New York (1949).

no association of solute molecules. Evidently separation of solute molecules by solvent is sufficient to prevent association for this compound.

It would be of interest to have viscosity data for other metal β-diketone chelates, to determine whether these also are associated in the liquid state. Several viscosity measurements were made on aluminium acetylacetonate at 193°C, immediately above its melting point. The value for the viscosity obtained, 2·74 cP, is considerably higher than the extrapolated value for aluminium *iso*valerylacetonate from Fig. 3.

TABLE 3.—DIELECTRIC CONSTANT DATA FOR ALUMINIUM *iso*VALERYLACETONATE

t (°C)	freq. (kc/s)	ϵ	P (cm)³	P (av.)	$P_E = MR_D$
26	3	2·99	174·7	173·8	131·0
	30	2·99	174·7		
	100	2·98	174·1		
	300	2·93	171·5		
50	3	2·92	174·5	173·9	
	30	2·91	173·9		
	100	2·91	173·9		
	300	2·90	173·4		
75	3	2·85	174·3	173·9	
	30	2·85	174·3		
	100	2·84	173·7		
	300	2·83	173·2		
100	3	2·79	174·6	173·7	
	30	2·78	174·0		
	100	2·77	173·4		
	300	2·76	172·7		

From the viscosity and published density data, the rheochor for aluminium acetylacetonate at 193°C is calculated to be 364. A maximum rheochor value of 520 may be taken as the limit toward which the curve appears to be approaching in Fig. 5.* If 520 can be taken to be equal to the rheochor characteristic of unassociated aluminium *iso*valerylacetonate, it would be possible to calculate a rheochor value for unassociated aluminium acetylacetonate, using this value and the atomic rheochor increments for C and H listed by FRIEND. The value 306, calculated in this way, is much smaller than the observed value 364, indicating that aluminium acetylacetonate is also associated at the temperature of measurement.

Dielectric measurements

The dielectric constant of liquid aluminium *iso*valerylacetonate was determined over a range of temperature and frequencies. The results are listed in Table 3. Polarization values calculated from equation (2) are listed in column 4 of this table.

* The limit is probably somewhat lower than 520. This would lead to an even lower calculated value for the rheochor of aluminium acetylacetonate than that given in the text.

These values appear to decrease slightly with increasing frequency. The magnitude of the variation, however, scarcely exceeds experimental error. The P values at each temperature have accordingly been averaged and the resulting values listed in column 5 of Table 3. It is seen that P(av.) is independent of temperature, within the experimental error. This is good evidence that aluminium *iso*valerylacetonate possesses no permanent electric dipole moment; the latter conclusion is in agreement with the results which have been obtained for metal acetylacetonates in solution and in the vapour phase.[15,16]

The metal acetylacetonates have been shown to be non-polar, but to possess abnormally large atomic polarizations.[15,16] The difference, $P(\text{av.}) - P_E = 42{\cdot}8$ cm^3 (Table 3) represents the atomic polarization for aluminium *iso*valerylacetonate

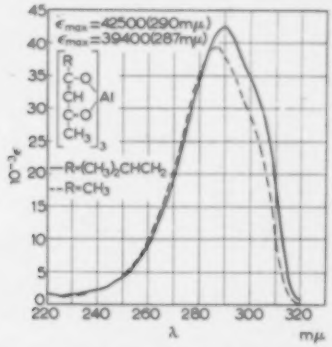
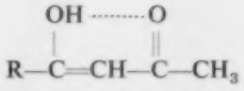


FIG. 6.—Ultra-violet absorption spectra of the aluminium chelates of *iso*valerylacetone, ————, and of acetylacetone, — — , in absolute ethanol.

in the liquid state. This compares very well with the atomic polarization values 42·9 and 39·7 cm^3 found for aluminium acetylacetonate in solution and in the vapour phase, respectively.[15,16] The present dielectric measurements appear to be the first for a metal β-diketone chelate in the liquid state.

Absorption spectra

The ultra-violet absorption spectrum of aluminium *iso*valerylacetonate is compared with that of aluminium acetylacetonate in Fig. 6. The two curves are very similar, indicating very similar structures for the two chelates, as would be expected. The value of ϵ_{max} for aluminium *iso*valerylacetonate is, however, greater than for aluminium acetylacetonate, and occurs at a longer wavelength. Both of these effects are probably related to the greater electron donating power of the $(CH_3)_2CHCH_2$ group to the chelate ring systems, relative to that of the methyl group. A similar increase in ϵ_{max} of the corresponding absorption bands for enolic β-diketones (II), as R is made more electron-repelling,



(II)

has been noted by BELFORD, MARTELL and CALVIN.[17]

[15] A. E. FINN, G. C. HAMPSON and L. E. SUTTON *J. chem. Soc.* 1254 (1938).
[16] I. E. COOP and L. E. SUTTON *J. chem. Soc.* 1269 (1938).
[17] R. L. BELFORD, A. E. MARTELL and M. CALVIN *J. inorg. nucl. Chem.* **2**, 11 (1956).

The ultra-violet spectra of metallic β-diketone chelates have been discussed in detail by the latter authors and by SONE.[18]

Acknowledgements—The writer is indebted to MISS M. RUTTER for the dielectric constant data and to MISS M. ARLENE DAVIS for help in obtaining the vapour-pressure results.

[18] K. SONE *J. Amer. chem. Soc.* **75**, 5207 (1953).

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J.Inorg. Nucl. Chem., 1958, Vol. 6, pp. 52 to 57. Pergamon Press Ltd., London

THE KINETICS OF EXCHANGE REACTIONS IN THE PRESENCE OF MULTIPLE EQUILIBRIA

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Abstract—Some expressions have been derived for the rate of isotopic exchange reactions in the presence of multiple equilibria. Chemical equilibria and the absence of isotopic effects are assumed. The implications of the results are illustrated with reference to the behaviour of several complex-ion systems.

THE general law which governs the rate of a simple isotopic exchange reaction was first derived by McKAY[1] and is applicable when two species in chemical equilibrium are involved, and provided certain other conditions are satisfied.[2] If, however, the concentration of a third active species becomes comparable with either of the other two, then the simple law no longer holds and others must be obtained.[3–6] We were interested in the question of exchange reactions in the presence of multiple equilibria in connexion with metal ammine exchange studies,[7–10] both from the point of view of ligand and central metal exchange. We have rigidly derived kinetic expressions for systems where three species only are involved and extended these to the more complicated situation involving more than three active species, since exact mathematical derivations in the latter case would be tedious. The discussion is always concerned with isotopic transfer with no net chemical reaction (i.e. chemical equilibria has been attained) and negligible isotope effect. The results will subsequently be discussed with reference to certain complex-ion systems.

METAL EXCHANGE

The equilibria involved are*

$$\begin{aligned} &MA_2 \overset{R_2}{\rightleftharpoons} MA + A \ldots k_2, k_{-2} \\ &MA \overset{R_1}{\rightleftharpoons} M + A \ldots k_1, k_{-1} \end{aligned} \qquad \text{(I)}$$

Let

$$\begin{aligned} M^*A_2 + MA_2 &= c & M^*A_2 &= c^* \\ M^*A + MA &= b & M^*A &= b^* \\ M^* + M &= a & M^* &= a^* \end{aligned}$$

* In this and in any subsequent discussion any charge is omitted for the sake of simplicity.

[1] H. A. C. McKAY *Nature* **142**, 997 (1938).
[2] D. R. STRANKS and R. G. WILKINS *Chem. Rev.* To be published.
[3] O. E. MYERS and R. J. PRESTWOOD *Radioactivity Applied to Chemistry* (Edited by WAHL and BONNER) Chap. 1. Wiley, New York (1951).
[4] R. L. WOLFGANG and R. W. DODSON *J. Amer. chem. Soc.* **76**, 2004 (1954).
[5] L. F. GRANTHAM, T. S. ELLEMAN and D. S. MARTIN, JR. *Ibid.* **77**, 2965 (1955).
[6] L. R. DARBEE, F. E. JENKINS and G. M. HARRIS *J. chem Phys.* **25**, 605 (1956).
[7] D. S. POPPLEWELL and R. G. WILKINS *J. chem. Soc.* 4098 (1955).
[8] R. G. WILKINS and M. J. G. WILLIAMS *Ibid.* 1763 (1957).
[9] R. G. WILKINS and M. J. G. WILLIAMS *Ibid.* 4514 (1957).
[10] R. G. WILKINS *Ibid.* 4521 (1957).

where an asterisk denotes a labelled atom and R_2 and R_1 are the rates of the chemical reactions leading to exchange; k_2 and k_1 represent the forward and k_{-2} and k_{-1} the reverse reaction rate constants. It is assumed that the two reactions in (I) represent the only path for exchange (for example, there is no direct bimolecular exchange between M and MA_2). Then

$$\left.\begin{aligned} -\frac{dc^*}{dt} &= R_2\left(\frac{c^*}{c}-\frac{b^*}{b}\right) \\ -\frac{da^*}{dt} &= R_1\left(\frac{a^*}{a}-\frac{b^*}{b}\right) \\ a^*+b^*+c^* &= a_0^* = \text{constant} \end{aligned}\right\} \quad (1)$$

Such differential equations are similar to those of MYERS and PRESTWOOD[3] (who treated the case of competitive exchange reactions when two of the active species were present in the same molecule, but occupied positions of different reactivity), WOLFGANG and DODSON[4] (who treated the case of $R_1 = R_2$), and of GRANTHAM, ELLEMAN and MARTIN.[5] The equations are identical with those derived for competitive exchange reactions[6] which were solved for the initial condition, $t = 0$, $a^* = c^* = 0$, $b^* = b_0^*$. We were interested in labelled metal ion exchanges, i.e. $t = 0$, $b^* = c^* = 0$, $a^* = a_0^*$ and the solution is

$$c^* = c_\infty^* - c_\infty^*\left[\left(\frac{\theta-\phi}{2\theta}\right)\exp\left\{-\frac{t}{2}(\theta+\phi)\right\}+\left(\frac{\theta+\phi}{2\theta}\right)\exp\left\{-\frac{t}{2}(\phi-\theta)\right\}\right] \quad (2)$$

$$a^* = a_\infty^* + \frac{1}{\theta}\left[\left\{\frac{(a_0^*-a_\infty^*)(\theta-\phi)}{2}+\frac{R_1a_0^*}{a}\right\}\exp\left\{-\frac{t}{2}(\theta+\phi)\right\}\right.$$
$$\left.+\left\{\frac{(a_0^*-a_\infty^*)(\theta+\phi)}{2}-\frac{R_1a_0^*}{a}\right\}\exp\left\{-\frac{t}{2}(\phi-\theta)\right\}\right] \quad (3)$$

where $a_\infty^* = \dfrac{a_0^*a}{a+b+c}$; $c_\infty^* = \dfrac{a_0^*c}{a+b+c}$; $\phi = \left(\dfrac{R_1}{b}+\dfrac{R_1}{a}+\dfrac{R_2}{c}+\dfrac{R_2}{b}\right)$

$$\theta = \left[\left\{R_2\left(\frac{1}{b}+\frac{1}{c}\right)-R_1\left(\frac{1}{a}+\frac{1}{b}\right)\right\}^2+\frac{4R_1R_2}{b^2}\right]^{\frac{1}{2}}$$

and subscripts 0 and ∞ refer to values at zero-time and at the completion of exchange.

An examination of equations (2) and (3) shows that it is unlikely when equilibria like (I) are involved that straight-line plots of $\ln[1-(c^*/c_\infty^*)]$ against time t will result. With certain conditions, however, such a simple relationship will hold.

Limiting forms. (a) $b \ll a,c$. Equation (3) can be shown to reduce to (4), the equation for a simple exchange:

$$\ln\left[1-\frac{a_0^*-a^*}{a_0^*-a_\infty^*}\right] = -\frac{R_1R_2}{R_1+R_2}\times\frac{(a+c)}{ac}t \quad (4)$$

This equation can also be obtained by using the steady state condition $db^*/dt = 0$ before integrating in (I). Equation (4) is a particular case of the MCKAY equation,

where R the rate of the chemical reaction leading to exchange equals $R_1R_2/(R_1 + R_2)$ and has been deduced by TAUBE.[11]

(b) $R_2 \gg R_1$. It can be shown[3,12] by putting $b^* = c^*$ at all times in equation (1) that:

$$\ln\left[1 - \frac{a_0^* - a^*}{a_0^* - a_\infty^*}\right] = -R_1 \frac{(a+b+c)}{(b+c)a} t \tag{5}$$

and obviously if $R_1 \gg R_2$ a similar equation will apply.

Even when these limiting forms are not applicable, by using equations (1) directly it is possible to estimate the values of R_1 and R_2 by measuring the specific activities of MA_2, MA, and M at various values of t. Such a procedure has been used, for example, in metal exchange studies involving $[Ni\ phen_2]^{2+}$, $[Ni\ phen]^{2+}$, and Ni^{2+} species,[9] (phen = 1 : 10 phenanthroline).

LIGAND EXCHANGE

The pertinent equilibria are the same as represented in (I). Now we have

$$MA_2 + MA^*A + MA_2^* = c \qquad MA^*A + 2MA_2^* = c^*$$
$$MA + MA^* = b \qquad MA^* = b^*$$
$$A + A^* = a \qquad A^* = a^*$$

It is easily seen that

$$\left.\begin{aligned} -\frac{dc^*}{dt} &= R_2\left(\frac{c^*}{c} - \frac{b^*}{b} - \frac{a^*}{a}\right) \\ -\frac{da^*}{dt} &= R_2\left(\frac{a^*}{a} - \frac{c^*}{2c}\right) + R_1\left(\frac{a^*}{a} - \frac{b^*}{b}\right) \\ a^* + b^* + c^* &= a_0^* \end{aligned}\right\} \tag{6}$$

Solving for c^* if $b^* = c^* = 0$ at $t = 0$, we obtain

$$c^* = c_\infty^* - \left[\frac{(2R_2a_0^*/a) + c_\infty^*(\theta+\phi)}{2\phi}\right] \exp\left\{-\frac{t}{2}(\theta-\phi)\right\} + \left[\frac{(2R_2a_0^*/a) + c_\infty^*(\theta-\phi)}{2\phi}\right] \exp\left\{-\frac{t}{2}(\theta+\phi)\right\} \tag{7}$$

where $c_\infty^* = \dfrac{2a_0^*c}{a+b+2c}$, $\qquad \theta = \left(\dfrac{R_2}{a} + \dfrac{R_2}{b} + \dfrac{R_2}{c} + \dfrac{R_1}{b} + \dfrac{R_1}{a}\right)$

$$\phi = (\theta^2 - 4\gamma)^{\frac{1}{2}} \quad \text{and} \quad \gamma = \frac{R_2(R_2+2R_1)}{2abc}(a+b+2c)$$

Once again limiting forms are possible:

Limiting forms. (c) $b \ll a,c$. Equation (7) then becomes

$$\ln\left(1 - \frac{c^*}{c_\infty^*}\right) = -\frac{R_2(R_2+2R_1)}{(R_1+R_2)} \cdot \frac{(a+2c)}{2ac} t \tag{8}$$

[11] H. TAUBE *Chem. Rev.* **50**, 69 (1952).
[12] H. M. NEUMANN and H. BROWN *J. Amer. chem. Soc.* **78**, 1843 (1956).

Equation (8) may also be derived as in metal exchange by assuming $db^*/dt = 0$ in equation (6). Simpler forms still may be obtained if $R_2 \gg R_1$ or $R_1 \gg R_2$.

(d) $R_1 = 0$. The equation for c^* will be the same as (7) except that now

$$\phi = R_2\left[\frac{1}{c^2} + \left(\frac{1}{b} - \frac{1}{a}\right)^2\right]^{\frac{1}{2}}, \qquad \theta = \left(\frac{1}{a} + \frac{1}{b} + \frac{1}{c}\right)R_2.$$

In this case when $b \ll a, c$ we have the simpler form:

$$\ln\left(1 - \frac{c^*}{c_\infty{}^*}\right) = -R_2\left(\frac{a + 2c}{2ac}\right)t \tag{9}$$

(e) $R_1 \gg R_2$. For this case,

$$\ln\left(1 - \frac{c^*}{c_\infty{}^*}\right) = -\frac{R_2(a + b + 2c)}{2c(a + b)}\,t \tag{10}$$

Extension to higher complexes. The general solution in the case of exchanges involving higher complexes (e.g. MA_3 see (II)) would be complicated.

$$\begin{aligned} MA_3 &\overset{R_3}{\rightleftharpoons} MA_2 + A \ldots k_3, k_{-3} \\ MA_2 &\overset{R_2}{\rightleftharpoons} MA + A \ldots k_2, k_{-2} \\ MA &\overset{R_1}{\rightleftharpoons} M + A \ldots k_1, k_{-1} \end{aligned} \tag{II}$$

However, the limiting cases are of interest when $[MA_2]$, $[MA]$, $[A] \ll [MA_3]$, $[M]$ in metal exchange and when $[MA_2]$, $[MA]$, $[M] \ll [MA_3]$, $[A]$ in ligand exchange. If we assume for the former that $d[M^*A_2]/dt \sim d[M^*A]/dt \sim 0$, the normal McKay equation follows with R, the rate of the chemical reaction leading to metal exchange, given by

$$R = \frac{R_1R_2R_3}{(R_1R_2 + R_2R_3 + R_1R_3)} \tag{11}$$

For ligand exchange, it follows from equations (8) and (11) that

$$R = R_3 + \frac{R_3R_2}{R_3 + R_2} + \frac{R_1R_2R_3}{R_1R_2 + R_2R_3 + R_1R_3} \tag{12}$$

DISCUSSION

It is obvious from the above that the presence of a third active species will often cause deviations from linearity of McKay plots (equations (2), (3) and (7)) but that these disappear when $b \ll a, c$ (equations (4), (8), and (9)). The question of metal exchange has been dealt with by Taube[11] and will not directly be referred to further here. Considering (II) and combining equations (11) and (12),

$$R_{\text{ligand}} = R_3 + \frac{R_3R_2}{R_3 + R_2} + R_{\text{metal}}$$

where R_{metal} would refer to metal exchange with conditions exactly like those for ligand exchange. In Table 1 are collected R values which would be observed in

tris-complex exchanges for various relative values of R_1, R_2, and R_3. They are easily deduced from equations (11) and (12).

The simplest case, and the one with which we are invariably concerned, occurs when a ligand exchange rate is first order in complex concentration and zero order in ligand concentration, $R_{lig} = k_{lig}[MA_3]$. Any of the first three entries in Table 1 could

TABLE 1

Relative rates	R_{ligand}	R_{metal}
$R_3 \ll R_1, R_2$	$3R_3$	R_3
$R_1 \ll R_3 \ll R_2$	$\sim 2R_3$	$\ll R_3$
$R_2 \ll R_3$	$\sim R_3$	$\ll R_3$
$R_1 \sim R_2 \sim R_3$	Functions of all rates given by equations (11) and (12)	

yield this result and so correlation of R_{lig} unambiguously with R_3, $2R_3$, or $3R_3$ is not possible. It follows therefore for ligand exchange that $3k_3 \geqslant k_{lig} \geqslant k_3$. In the exchange of phenanthroline with [Ni $phen_3$]$^{2+}$ which has been shown to be first order in complex and zero order in phenanthroline concentration,[8] it can be shown that $k_{lig} = k_3$, with the conditions of ligand exchange, from other exchange experiments.[9]

In both radioactive metal and ligand exchange studies with [Ni $tetraMeen_2$]$^{2+}$ (tetraMeen = tetra C-methylethylenediamine) at pH 6·8 it was found that the exchange rates $R_{lig} = k_{lig}$ [complex] and $R_{metal} = k_{metal}$ [complex].[10] The value of $k_{lig} = 2k_{metal} = 2k_2$ (see I) and obviously with this system the relationship $R_1 \gg R_2$ applies even with ligand exchange where the conditions favour a small concentration of [M tetraMeen]$^{+2}$. The relationship between k_{lig}, k_{metal}, and k_2 follows from a consideration of equations (4) and (8). Another example where subsequent dissociative stages are also faster than the initial one is probably afforded by the $AuCl_4^-$, Cl^{*-} exchanges.[13] The [Fe $phen_3$]$^{2+}$, phen* exchange displays properties of both the above.[14] Once again in neutral solution $R = k_{lig}$ [complex] and the value of k_{lig} can be equated with k_3 (i.e. R_1, $R_2 \ll R_3$), but in 0·1 M HCl the ligand exchange rate constant now has a value *three* times that in neutral solution and now R_1, $R_2 \gg R_3$. This circumstance can arise because the dissociative rate constants and the concentrations of [Fe $phen_2$]$^{2+}$ and [Fe phen]$^{2+}$ may be markedly increased in acid. Certainly the dissociation of [Ni phen]$^{2+}$ but not [Ni $phen_2$]$^{2+}$ is acid-catalysed.[15] The exchanges involving [Fe $dipy_3$]$^{2+}$ and dipyridyl show similar characteristics.[16] Moreover, in neutral solution the value for k_{exch} *increases* as the concentration of dipyridyl *decreases*. We interpret this to mean that as the concentration of dipyridyl decreases, the concentrations at chemical equilibria of the bis- and mono-species will increase as will also $R_2(=k_2$[Fe $dipy_2^+$]) and $R_1(=k_1$[Fe $dipy^{2+}$]); for some intermediate dipyridyl concentration the fourth condition of Table 1 will hold. Such considerations as the

[13] R. L. RICH and H. TAUBE *J. phys. Chem.* **58**, 1 (1954).
[14] R. G. WILKINS and M. J. G. WILLIAMS Unpublished observations.
[15] D. W. MARGERUM, R. I. BYSTROFF and C. V. BANKS *J. Amer. chem. Soc.* **78**, 4211 (1956).
[16] P. ELLIS and R. G. WILKINS Unpublished observations.

above may provide a partial explanation of the results of WHITNEY, SCHWEITZER and COMAR,[17] who found peculiar rate dependences for the Fe $phen_3^{2+}$ and Fe $dipy_3^{2+}$ — Fe^{2+} exchanges in weakly acid solution. Generally, we may say that for an exchange where two species predominate if two or more steps are rate-determining complicated kinetics will result which will probably be of non-integral order in the bulk reactants.[18]

Acknowledgements—The authors wish to thank the Department of Scientific and Industrial Research for a maintenance grant (to M. J. G. W.). They are grateful to Professor A. W. ADAMSON, who read the manuscript and made helpful comments and criticisms.

[17] I. B. WHITNEY, G. K. SCHWEITZER and C. L. COMAR *J. Amer. chem. Soc.* **77**, 1390 (1955).
[18] J. EGGERT *Physical Chemistry* (Translated by S. J. GREGG) p. 520. Constable, London (1932).

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ANION EXCHANGE STUDIES OF SC(III) AND V(IV). SEPARATION OF SCANDIUM, TITANIUM AND VANADIUM*

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Abstract—The adsorption on Dowex-1 anion exchange resin of Sc(III) and V(IV) tracers has been studied in the presence of low concentrations of oxalate, citrate, fluoride, and carbonate ions. V(IV) forms strongly adsorbed complex anions with each of these reagents, as does Sc(III) with the first two. Both tracers are strongly adsorbed from oxalic acid solution, and their oxalate complexes are selectively destroyed by the addition of hydrochloric acid. These data have been used as the basis of a method for the anion exchange separation of Sc(III), V(IV), and Ti(IV) in oxalic acid–hydrochloric acid mixtures.

THE chemical literature contains scattered observations of the ion exchange properties of scandium, vanadium, and titanium. The cation exchange of Sc(III) in the presence of a variety of complexing anions has been reported,[1] and VICKERY[2] has demonstrated that Sc(III) in citrate or oxalate solution is adsorbed on an anion exchange resin. The cation exchange of V(IV) and V(V) has been reported,[3] as has its anion exchange in the presence of citrate.[4] V(IV) shows only slight absorption from hydrochloric acid solutions in the concentration range 1–12 M; V(V) is strongly adsorbed as an anion from the 12 M acid, but is reduced rapidly on the resin by this high concentration of chloride ion.[5] Ti(IV) is weakly adsorbed as an anion from 5 per cent HF–10 per cent HCl mixtures,[6] and is also adsorbed from 9–12 M hydrochloric acid.[5] Hydrochloric acid affords a potential solvent for the separation of V(IV) and Ti(IV) on Dowex-1 resin by retention of the latter while the former passes through the column. Relatively long columns are required, and the available data do not make clear how Sc(III) (which is weakly adsorbed from 12 M acid) would fit into the scheme, or whether widely disproportionate amounts of these elements could conveniently be separated.[5] Since no studies except those in hydrochloric acid of the three elements in a common solvent-complexing agent system have been made, the survey of anion exchange properties reported here was undertaken to obtain information which would afford a method for the sharp separation of Sc, V and Ti.‡

* This work was carried out under the auspices of the U.S. Atomic Energy Commission.

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‡ As this report was being prepared, an abstract has become available which states that a method has been worked out for the separation of these and other elements of the fourth period: F. NELSON and K. A. KRAUS, Abstracts of Papers, 131st Meeting, American Chemical Society, Miami, Florida; April, 1957, p. 14M. Their procedure for separating Sc and V evidently is essentially similar to that reported here, but with ethylenediaminetetraacetic acid used as the chelating agent, instead of oxalic acid.

Still another separation is described in a preprint (kindly furnished by the authors) by U. SCHINDEWOLF and J. W. IRVINE, JR. *Analytical Chemistry* (to be published.) Sc, V and Ti are separated by anion exchange from 0·5 to 15 M HF solution.

(1) V. K. IYA *C. R. Acad. Sci., Paris* **236**, 608 (1953); V. K. IYA and J. LORIERS *Ibid.* **237**, 1413 (1953); P. RADHAKRISHNA *Analyt. chim. Acta* **8**, 140 (1953).
(2) R. C. VICKERY *J. chem. Soc.* 245 (1955).
(3) H. KAKIHANA *Bull. chem. Soc. Japan* **22**, 242 (1949), and J. E. SALMON and H. R. TIETZE *J. chem. Soc.* 2324 (1952).
(4) O. SAMUELSON, *Z. Elektrochem.* **57**, 207 (1953).
(5) K. A. KRAUS, F. NELSON and G. W. SMITH *J. phys. Chem.* **58**, 11 (1954).
(6) J. L. HAGUE, E. D. BROWN and H. A. BRIGHT *J. Res. nat. Bur. Stand.* **53**, 261 (1954).

EXPERIMENTAL

Data on the anion exchange behaviour of Sc(III) and V(IV) were obtained by both the column and equilibrium methods described by KRAUS *et al.*[5] The resin used was Dowex-1, a quarternary amine polystyrene-divinylbenzene (ca. 10 per cent) anion exchanger. The finer material in the 100–200-mesh range was removed by decanting from a partially settled suspension of the resin, and the coarse residue used for this work. Since a number of different complexing anions were to be surveyed, the commercial resin, which is furnished as the chloride, was converted to the formate by washing a large column with sodium formate until chloride was no longer detected in the eluate; the product was dried in air. Formate ion is weakly held by the resin,[7] and should not interfere with exchange equilibria involving other more strongly adsorbed anions. When this air-dried resin was dried to constant weight in vacuum at 60° C over anhydrone, the weight loss averaged 16 per cent. Weights of air-dried resin were converted to the dry weight before calculating the adsorption data.

Tracer solutions containing ^{46}Sc(III) or ^{48}V(IV) were made up from activities produced by deuteron bombardment of titanium metal in the Brookhaven cyclotron. The adsorption data reported here were obtained with solutions in 10^{-4} M formic acid of ca. 10^{-12}–10^{-13} M tracer activities separated by the ion-exchange procedure reported below; these stock solutions were diluted 1 : 5 with solutions of the complexing anions. The scandium stock solutions deposited activity on the container walls on standing, but aliquots could be pipetted reproducibly within 1 per cent from new or freshly-filtered old solutions if the work was carried out rapidly. The vanadium solutions were quite stable. Identity of each activity was confirmed by determining the gamma-ray photopeak energies with a hundred-channel pulse-height analyser, using neutron-produced ^{46}Sc and ^{60}Co standards. Concentrations of the tracers in samples equilibrated with resin were determined by counting the solutions directly in a well-type sodium iodide scintillation counter.

In the equilibration experiments, tracer samples were shaken for 110 hr in cellulose acetate vials with weighed amounts of Dowex-1 formate in 5·00 ml of solution containing one of the solutes studied. The solution was sampled for counting after centrifuging down the resin; no filterable activity was found in any sample counted. Activity adsorbed on vial walls was removed and counted by washing with 6 M hydrochloric acid. The data are given in Fig. 1 in the form of distribution coefficients, where D is defined as: activity per kilogram of dry resin ÷ activity per litre of solution.*

Column experiments were used to determine the rate of elution of Sc(III) from oxalic acid–hydrochloric acid solutions. Scandium is weakly held under these conditions, so the distribution coefficients in Table 1 were calculated from the column data, using the relation:[8]

$$D = \frac{V_m - i}{\rho}.$$

V_m is the number of column-volumes of wash solution required to reach the elution maximum, and for the resin used, both i, the fractional interstitial volume, and ρ,

* A referee has pointed out that since the effect of wide variation in resin weights was not checked, there is a possibility that surface adsorption also occurs in the systems reported.

[7] R. W. WHEATON and W. C. BAUMAN *Ind. eng. Chem.* (*Industr.*) **43**, 1088 (1951).
[8] F. NELSON and K. A. KRAUS *J. Amer. chem. Soc.* **77**, 801 (1955).

the resin-bed density, had the value 0·4. Since no titanium isotope with a convenient half-life is known, data on Ti(IV) were collected only for the oxalic acid–hydrochloric acid mixtures from column experiments, either by following the pale yellow band visually, or by spectrophotometric determination of the peroxide complex. In all of these experiments, the column length was 10 cm, and its cross-section 0·209 cm². A column of the same dimensions was used for the separation demonstrated in Fig. 2.

An advantage in the use of oxalic acid as the chelating agent for the anion-exchange

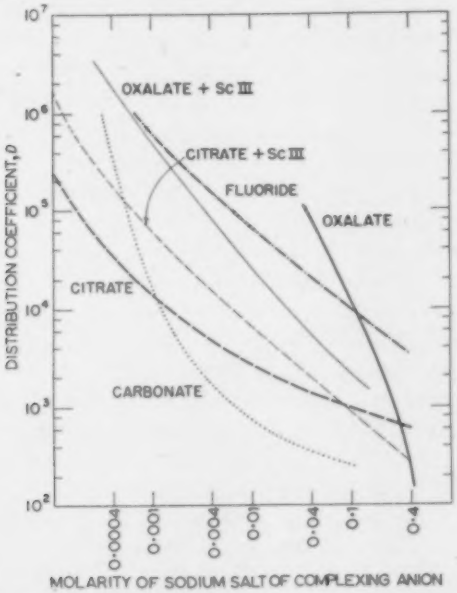

FIG. 1.—Variation in the distribution of Sc(III) (narrow lines) and V(IV) (heavy lines) between Dowex-1 resin and solution, as a function of concentration of chelating agent. The solutes indicated by the various curves are oxalate (solid lines), citrate (dashed lines), carbonate (dotted line), and fluoride (dot–dash line).

separation of Sc(III) and V(IV) arises from the fact that these tracers can easily be recovered free of other solutes from column eluates containing only hydrochloric and oxalic acids. The procedure involves evaporation to dryness (to remove hydrochloric acid, which catalyses the decomposition of hydrogen peroxide), followed by heating with a solution containing excess hydrogen peroxide to destroy the oxalic acid. In the case of vanadium solutions, the activity is volatile when heated strongly in the presence of oxalic acid. To avoid loss, evaporation of hydrochloric acid must be carried out slowly, and the subsequent treatment with hydrogen peroxide must be carried out with sufficient excess of that reagent to ensure destruction of all of the oxalic acid before the solution evaporates to dryness.

Solutions of the complexing solutes were made up from reagent-grade sodium salts. No effort was made to maintain constant ionic strength through a series of concentrations of a given solute.

RESULTS

Adsorption of Sc(III), Ti(IV) *and* V(IV)

The distribution coefficients plotted in Fig. 1 indicate strong adsorption of Sc(III)

from dilute citrate and oxalate solutions, and of V(IV) from carbonate, fluoride, citrate, and oxalate. In most cases the data were not reproducible at 0·0001 M concentration of the complexing solute (the lowest concentration studied in each case), but could be duplicated within a factor of 2 or better at the higher concentrations. The results for Sc(III) in carbonate and fluoride were quite erratic. These samples failed to approach equilibrium with the resin smoothly with increased shaking time

TABLE 1.—ADSORPTION OF Sc(III) AND V(IV) ON DOWEX-1 FROM 0·1 M OXALIC ACID–HYDROCHLORIC ACID MIXTURES

Concentration of HCl in mixture	0	0·01 M	0·04 M	0·1 M	0·4 M
D for V(IV)	300,000	300,000	14,000	2400	40
D for Sc(III)	8100	—	400	60	8

up to 110 hr, and they deposited a large fraction (up to half) of the total activity on the walls of the vials in which they were shaken. The samples which gave the data reproduced in Fig. 1 did not show either of these difficulties, which probably are indicative of radiocolloid formation. Instead, they came to equilibrium with the resin within 60 hr, and deposited less than 2 per cent of the total activity on the vial walls. It is worth noting that the Sc(III)-fluoride system always showed a minimum *D*-value in the range 0·001 to 0·004 M fluoride, although the value of *D* at the minimum and its position varied from sample to sample. The data for V(IV) in oxalate were erratic for oxalate concentrations below 0·04 M, but in this case the indications of radiocolloid formation observed for Sc samples were absent. It seems more probable that the difficulty in this case was due to failure to reach equilibrium with the resin at very high *D*-values (ca. 10^6) in the shaking times used.

Reproducible data were obtained for both Sc(III) and V(IV) in oxalic acid–hydrochloric acid mixtures. Addition of the latter acid permits selective and much more rapid elution of these ions from the column, presumably by the stepwise destruction of the adsorbed anionic species. Sc(III) is weakly adsorbed in the presence of hydrochloric acid; the distribution constants for it in Table 1 were calculated from data obtained by the column method. V(IV) is more strongly adsorbed, and data for it were obtained by the equilibration method. Ti(IV) is so strongly retained in the presence of oxalate that no data could be obtained, and the yellow band could be eluted only by washing with 0·1 M hydrochloric acid. Since elution required 3·5 column volumes of the acid, the Ti(IV) possibly is weakly adsorbed from this solution.

Separation of Sc(III), V(IV) *and* Ti(IV)

The distribution data plotted in Fig. 1 offer little prospect for an effective anion-exchange separation of Sc(III) and V(IV). Carbonate and fluoride cannot be used as complexing agents for the former, and distribution coefficients for the two citrate systems are too much alike to afford a useful method. The oxalate systems, which might be useful at the lower concentrations of oxalate ion, are eliminated by the erratic behaviour of V(IV).

The data for Sc and V in Table 1, on the other hand, differ substantially, and afford a method for the separation of these two ions and Ti(IV). Such a separation is illustrated in Fig. 2. A solution in 0·1 M oxalic acid of scandium and vanadium tracers and 5 mg Ti(IV) was passed through a column 10 cm long and 0·209 cm² in

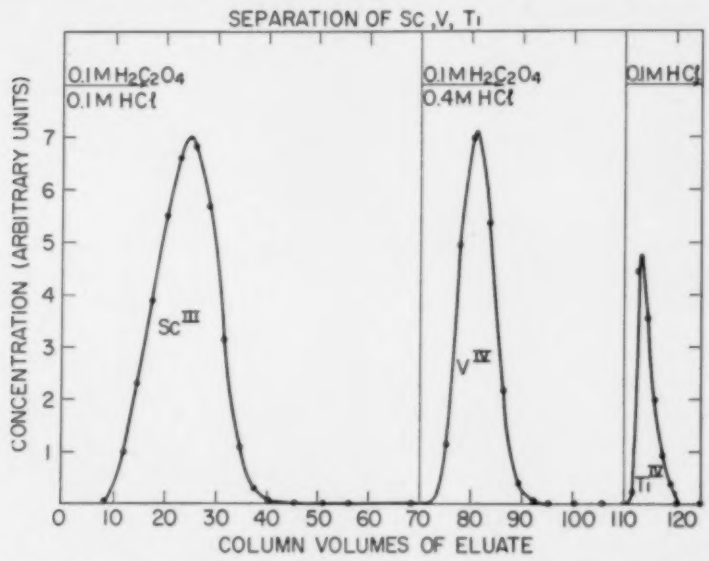

FIG. 2.—Separation of Sc(III), V(IV), and Ti(IV) by ion exchange from oxalic acid–hydrochloric acid mixtures.

cross-section. All three ions were retained in a narrow band at the top of the column. Washing with a solution 0·1 M in both oxalic and hydrochloric acids eluted Sc(III). Change of the wash solution to 0·1 M oxalic–0·4 M hydrochloric acids eluted V(IV). The titanium band was still at its original position at the top of the column, and was eluted in a small volume of 0·1 M hydrochloric acid. Essentially the same separation was achieved on the same column when a mixture containing 5 mg of each ion, with added Sc(III) tracer to mark the position of that colourless band, was passed through the column with the same series of wash solutions. Average flow rate of all solutions was 0·5 ml/min.

Acknowledgements—The author is indebted to Drs. K. A. KRAUS and F. NELSON of the Oak Ridge National Laboratory, for a helpful discussion of their techniques for study of ion-exchange equilibria. It is a pleasure to acknowledge the hospitality of Dr. V. W. COHEN of the Brookhaven National Laboratory, in whose laboratory this work was carried out.

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PREPARATION OF CARRIER-FREE SCANDIUM AND VANADIUM ACTIVITIES FROM TITANIUM CYCLOTRON TARGETS*

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Abstract—A method is described for the separation in high yields of carrier-free ^{46}Sc and $^{48,49}V$ activities from deuteron-bombarded titanium cyclotron targets. The procedure involves distillation of V and Ti chlorides (with Sc and Ca chlorides left behind), separation of V from solution in refluxing $TiCl_4$ on a fresh CuCl surface, and removal of milligramme amounts of Ti by ion exchange.

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WHEN titanium metal is bombarded by deuterons in the cyclotron, a mixture of calcium, scandium, and vanadium activities is produced by (d, α), $(d, 2n)$, and (d, n) reactions on the isotopic mixture of natural titanium.[1] Carrier-free ^{46}Sc has been separated in high yield from the titanium by filtration of the Sc radiocolloid formed when ammonia is added to a solution of the titanium peroxide complex.[2] Vanadium activity has been separated by precipitation (with added carrier?) as $Pb(VO_3)_2$.[3] Carrier-free vanadium activity has been separated from the residue remaining after fuming dry a sulphuric acid solution of the titanium target by the sequence: carbonate fusion, extraction of vanadate, and scavenging with calcium and scandium carbonates.[4] A very convenient separation has been developed simultaneously with our work by SCHINDEWOLF and IRVINE,‡ who dissolved their target in hydrofluoric acid, and separated the activities in this solution by anion exchange from 0·5 to 15 M hydrofluoric acid solutions. They worked with 1 g of titanium target, and their ion-exchange separation would involve rather cumbersome solution volumes with the larger amounts of target (6–10 g) used in our work. The new separation method reported here was developed to meet a requirement for a procedure suitable for preparing large amounts of carrier-free vanadium activity in a form free of complexing anions, from titanium targets in the 20–100 r range. It is worth noting that strictly carrier-free vanadium activity cannot be prepared from commercially available titanium; the best (iodide process) grades of the metal contain about 10 p.p.m. of ^{51}V as an impurity.

EXPERIMENTAL

The train in which the preliminary separation of titanium was carried out is illustrated in Fig. 1. Titanium and vanadium react with chlorine at 400°C in F to give

* This work was carried out under the auspices of the U.S. Atomic Energy Commission.
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‡ The author is indebted to Prof. J. W. IRVINE, JR., for a preprint of the paper describing this separation, which is to be published in *Analytical Chemistry*.

[1] G. T. SEABORG and I. PERLMAN *Rev. mod. Phys* **20**, 585 (1948).
[2] J. D. GILE, W. M. GARRISON and J. G. HAMILTON *J. chem. Phys.* **18**, 1685 (1950).
[3] R. W. HAYWARD and D. D. HOPPES *Phys. Rev.* **104**, 183 (1956).
[4] H. R. HAYWARD, R. D. MAXWELL, W. M. GARRISON and J. G. HAMILTON *J. chem. Phys.* **18**, 756 (1950).

$TiCl_4$ and VCl_4 (or possibly $VOCl_3$), which distil off into *T*-I at the reaction temperature. $ScCl_3$ and $CaCl_2$ remain behind. Coloured impurities in the $TiCl_4$ are removed by redistillation into *T*-II. Vanadium then separates from solution in refluxing liquid $TiCl_4$ on the surface film formed on copper paddle *P* immersed in the liquid. This procedure has been used industrially[5] and in the laboratory[6] for removal

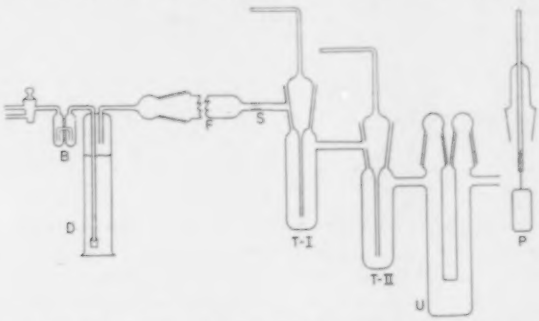

FIG. 1. Apparatus for the preparation and distillation of $TiCl_4$, and for the separation of dissolved vanadium from the distillate. Helium or hydrogen gas is admitted through the stopcock, bubbler *B*, and drying tower *D*. Vycor furnace tube *F* is connected through a graded seal *S* to the Pyrex trap system. Traps *T*-I and *T*-II are made from 6 mm right-angle vacuum stopcocks. The U-tube is filled with glass wool, and connected to a drying tube. All horizontal connexions beyond *S* should slope downward to facilitate drainage of $TiCl_4$. Copper paddle *P* is mounted as shown on a 24/40 joint which can replace the stopcock plug of either trap, and simultaneously seals the inlet to it.

of vanadium in the purification of $TiCl_4$. The activity is removed from the paddle by immersion in dilute HCl, and final purification carried out by an ion-exchange process.

In operating the line, the cyclotron target (with dimensions ca. 2·5 × 15 cm after trimming, and weight 6–10 g) was folded lengthwise into a V-shape in a wooden jig, slipped into the furnace, and the ground joint sealed with Apiezon *W*. The system was swept with helium, while the furnace tube was heated to 400°C. Then trap I was cooled with ice, and II with dry ice, while chlorine was passed through the line until the target was completely converted to $TiCl_4$, which condensed in trap I. The furnace was then allowed to cool, the second trap warmed to room temperature, and the system swept slowly with helium to remove condensed Cl_2 from trap II. The $TiCl_4$ in trap I was dark brown, and contained a good deal of ^{46}Sc activity carried over mechanically from the furnace. By rotating the stopcock plug in I, the inlet was closed off and the $TiCl_4$ could be distilled into II, where it condensed as a pale yellow liquid.

A copper paddle was cleaned by heating to dull redness and immersing in methanol, dried, and inserted in trap II in place of the stopcock plug. When the $TiCl_4$ was refluxed, the surface of the copper became dark brown, and ^{48}V activity deposited on it. Two paddles immersed for 30 min each in the refluxing $TiCl_4$ removed ^{48}V activity quantitatively from the liquid. (Some ^{46}Sc activity remained in the solution.) The paddles were rinsed in CCl_4 immediately after removal from the $TiCl_4$, and then immersed in 1 M hydrochloric acid. The activity dissolved, together with more or

[5] U.S. Patent 2, 530, 735, *Chem. Abstr.* **45**, 2162h (1951); U.S. Patent 2, 600, 881, *Chem. Abstr.* **46**, 11605b (1952).
[6] W. S. CLABAUGH, R. T. LESLIE and R. GILCHRIST *J. Res. nat. Bur. Stand.* **55**, 261 (1955).

less copper from the film on the metal surface. Copper was removed by precipitation of CuS from this hot solution with H_2S (to minimize scavenging by the CuC_2O_4 which otherwise would precipitate from oxalic acid solution), the solid filtered off, and the filtrate evaporated just to dryness. The dry residue was dissolved in 0·1 M oxalic acid, saturated with SO_2, and $^{48,49}V$ activity separated from tracer amounts of ^{46}Sc and milligramme amounts of titanium by ion exchange on Dowex-1,[7] using first a 1 × 15 cm column, followed by a second stage on a 0·5 × 5 cm column. Recovery of vanadium activity was estimated to be 80 per cent of that in the original target. Another 10 per cent was recovered by washing all apparatus beyond the furnace tube with 6 M HCl, evaporating to dryness, and separating an oxalic acid solution of the residue on the same ion-exchange columns. Oxalic acid was destroyed in the product by reaction with H_2O_2.

Two coloured bands which were not observed during trial separations of reagent chemicals appeared on the larger column used to separate target materials. One was a pale blue band which eluted somewhat faster than scandium; spectroscopic analysis* showed that copper was present in the dry residue. This band probably was the oxalate cupric complex described by Riley,[8] formed from copper introduced by oxidation of traces of CuS during washing of that precipitate. The other band was bright yellow and eluted erratically after the vanadium activity, so that it did not interfere with the separation. The substance causing this colour was not identified.

Most of the ^{46}Sc activity remained in the furnace tube, except for the small amount carried over mechanically with the $TiCl_4$. It was recovered by rinsing the furnace with hot 6 M hydrochloric acid. A known weight of oxalic acid was added, the filtered solution evaporated to dryness, and the residue taken up in enough water to give a solution 0·1 M in oxalic acid. The ^{46}Sc activity was then separated by ion-exchange.[7] Due to conversion of a small amount of the target to the oxide or nitride, which include ^{46}Sc mechanically, the recovery of this activity is variable, and is lower than the 95 per cent reported by Gile, Garrison and Hamilton.[2]

Radiochemical purity of the separated ^{46}Sc and $^{48,49}V$ activities was checked by following their decay curves, and by measurement of their gamma-ray energies. The photopeaks were located by means of a hundred-channel pulse height analyser (Radiation Instrument Development Laboratories) which was calibrated against neutron-produced ^{46}Sc and ^{60}Co. Only the gammas of a single species (0·89 and 1·12 MeV for ^{46}Sc, and 0·99 and 1·31 MeV for ^{48}V) were detected in any sample, and the photopeaks of the separated target scandium coincided with those of the neutron-bombarded scandium oxides. Both the beta and the gamma decay curves were checked, using month-old samples from which the shortest-lived activities had decayed away. (The longer-lived activities which might still have been present were 164 day ^{45}Ca, 85 day ^{46}Sc, 16·2 day ^{48}V, and 330 day ^{49}V.) Betas were counted in a flow counter (90 per cent argon–10 per cent methane gas) fitted with an aluminized Mylar window (ca. 1 mg/cm^2) and operating in the proportional range. The data were corrected for gamma counts by subtracting the count rate through a 200 mg aluminium absorber from that without absorber. Gamma counts were made with a sodium iodide-crystal

* The author is indebted to Mr. Morris Slavin of the Brookhaven Chemistry Department for the spectroscopic analyses.

[7] R. I. Walter *J. inorg. nucl. Chem.* **6**, 58 (1958).
[8] H. L. Riley *J. chem. Soc.* 1307 (1929).

scintillation counter and the same absorber. The scandium sample gave both beta and gamma decays with half-lives of 83 days over a period of five half-lives. The vanadium sample gave a gamma decay with a half-life of 16 days over ten half-lives. The beta counts, however, were a composite of a 16 day decay and a long-lived activity with a half-life of 320 $\pm$ 30 days. Absorption curves in beryllium and aluminium eliminated the possibility that this activity was due to the 0·25 MeV beta of ^{45}Ca. (It was estimated that ^{45}Ca activity equal to 0·05 per cent of the initial activity of sample would have been detected.) An X-ray energy determination with an X-ray proportional counter in conjunction with a pulse-height analyser confirmed that the long-lived activity was due to the 4·51 keV Ti X-ray which accompanies decay of ^{49}V; the peak was observed at 4·67 keV.*

DISCUSSION

The function of the copper metal in the vanadium separation is not clear from the literature.[5,6] The surface of the metal darkens when immersed in $TiCl_4$ (more rapidly if hot) only in the presence of vanadium. This purple–brown film could be removed by gentle scraping or by washing with water. It weighed about 1 mg/cm^2 of metal surface. Spectroscopic analysis† showed that copper was the only metal present in substantial amount. Gravimetric analysis for chloride was unsuccessful, because variable amounts of that ion were added to the solid film by hydrolysis of $TiCl_4$, which was incompletely removed by the CCl_4 rinse. An X-ray powder-photograph of a sample (dried in vacuum over P_2O_5) of the film gave a pattern which coincided with that of CuCl.‡ Evidently, then, the copper is oxidized to CuCl by the hot $TiCl_4$. Activity seemed to be picked up from the $TiCl_4$ over a longer time interval than that required for formation of the CuCl film. Furthermore, the film behaved erratically in 1 M HCl: sometimes it dissolved rapidly, and sometimes it failed to dissolve on standing overnight. Irrespective of this, the activity always dissolved quickly, and could be filtered off from the residue of inactive undissolved film. These qualitative observations suggest that the activity is *adsorbed on the surface* of the CuCl from solution in $TiCl_4$. The oxidation state of the vanadium recovered by this scheme is not known.

Solutions of ^{48}V (IV) were quite stable in the presence of reductants such as oxalic acid. Solutions of high specific activity without such solutes have been observed to undergo oxidation under conditions where inactive VO^{++} was stable. This behaviour suggests the occurrence of oxidation of tracer amounts of VO^{++} by products of the radiolysis of the solvent, in the absence of other reductants.

Acknowledgements—The author has had the benefit of helpful suggestions from more members of the Chemistry Department at Brookhaven than can be explicitly mentioned; Dr. W. RUBINSON in particular contributed a great deal by his patient advice on counting techniques. The work was carried out in the laboratory of Dr. V. W. COHEN; his constant co-operation is gratefully acknowledged. Dr. W. S. CLABAUGH of the National Bureau of Standards provided major help through a discussion of his use of copper metal to purify $TiCl_4$.

* Dr. JAMES CUMMING carried out this determination; the instrumentation used is described by W. RUBINSON and W. BERNSTEIN *Phys. Rev.* **86**, 545 (1952).

† See footnote to p. 65.

‡ Prof. G. L. ZIMMERMAN of Bryn Mawr College suggested this method for the identification, and helped with the analysis of the pattern obtained.

LETTERS TO THE EDITORS

Some observations on the preparation of neptunium oxides

(*Received* 9 *August* 1957)

THREE neptunium oxides have been reported: NpO, NpO_2 and Np_3O_8. NpO has only been prepared accidentally, during the formation of neptunium hydride.[1] NpO_2 is an apple-green or brown material, the product of ignition at 700–800°C in air of the hydroxide, peroxide, nitrate or oxalate of any oxidation state of neptunium,[2] and is isomorphous with UO_2 and PuO_2. Np_3O_8 is a chocolate brown compound and has been prepared by heating Np(IV), (V) or (VI) hydroxide in NO_2 at 300–400°C,[3,4] or by heating Np(V) and (VI) compounds in air at 275–300°C.[4] The temperature at which Np(V) hydroxide is dried appears to be critical in the formation of Np_3O_8.[2] The formula Np_3O_8 has been assigned on the basis of the composition $NpO_{2.66 \pm 0.02}$ determined by measurement of the oxygen evolved in decomposition to NpO_2.[4] Decomposition begins at 500°C and is essentially complete at 600°C.[4] Np_3O_8 is reported to be isomorphous with U_3O_8.[2,4]

The purpose of this communication is to report some data which support and extend the published information.

The starting material for these preparations was a solution of Np(V) nitrate in 1 M HNO_3, which had been highly purified by solvent extraction and ion exchange techniques. Np(V) hydroxide was precipitated from this solution by ammonia and washed with distilled water. The precipitates were normally dried in glass vessels and the ignition was carried out in platinum apparatus. Products were identified by their X-ray pattern.

The results of a considerable number of experiments are summarized in Table 1.

The formation of Np_3O_8 from Np(V) hydroxide has not hitherto been reported at as low a temperature as 150°C. The fact that an identical experiment led partially to the formation of NpO_2 emphasizes the critical nature of this low temperature treatment. Three hours at 600°C in air or argon was sufficient for complete decomposition to NpO_2, though at 500°C traces of Np_3O_8 were still visible after 6 hr. Some initial difficulty was experienced in identifying the chocolate-brown material as Np_3O_8. Despite the fact that it is reported to be isomorphous with U_3O_8, the X-ray pattern of the neptunium compound (Table 1, preparation 1) is appreciably different from that of U_3O_8 (Fig. 1). However, when the cell parameters given for Np_3O_8[5] were used to index the pattern, very good agreement was obtained between the observed and calculated *d* values. In Table 2 are listed the *d* values and their visual relative intensities, together with the Miller indices assigned for the first 29 lines.

The NpO_2 formed by ignition at 600°C was stable when heated in air at 1000°C or in hydrogen at 600°C. The normal (khaki) form of NpO_2 had a tap density of 1·2 g/cm³. The tap density of the black form, which has not, to our knowledge, been previously reported, was 5·2 g/cm³. Fig. 2 illustrates the structural relationship between UO_2, NpO_2 and PuO_2 as shown by their X-ray patterns.

[1] S. FRIED and N. R. DAVIDSON *J. Amer. chem. Soc.* **70**, 3539 (1948).
[2] B. B. CUNNINGHAM and J. C. HINDMAN *The Actinide Elements, National Nuclear Energy Series* Div. IV, Vol. 14a, Chap. 12. McGraw-Hill, New York (1954).
[3] G. GIBSON, D. M. GRUEN and J. J. KATZ *Report AECD* 2930 (1950).
[4] J. J. KATZ and D. M. GRUEN *J. Amer. chem. Soc.* **71**, 2106 (1949).
[5] R. C. L. MOONEY *Report ANL* 4031 (1947).

TABLE 1.—SUMMARY OF EXPERIMENTS ON THE PREPARATION OF NEPTUNIUM OXIDES

Experiment No.	Starting material	Treatment	Appearance of product	X-ray pattern of product
1	Np(V) hydroxide (wet)	16 hr at 150°C in air	Chocolate-brown powder	Np_2O_5
2	Np(V) hydroxide (dried at room temp)	3hr at 300°C in air	Chocolate-brown powder	Np_2O_5
3	Np(V) hydroxide (dried at room temp)	3 hr at 400°C in NO_2	Chocolate-brown powder	Np_2O_5 + unidentified lines
4	Np(V) hydroxide (wet)	16 hr at 150°C in air	Shiny black particles	NpO_2 + Np_2O_5
5	Np(V) hydroxide (dried at ~100°C)	1½ hr at 500°C in air	Chocolate-brown and khaki powders	NpO_2 + Np_2O_5
6	Np(V) hydroxide (dried at ~100°C)	6 hr at 500°C in air	Khaki powder with trace of chocolate-brown	NpO_2
7	Np(V) hydroxide (dried at ~100°C)	3 hr at 600°C in air	Khaki powder	NpO_2
8	Product of 5	2 hr at 600°C in air	Khaki powder	NpO_2
9	Product of 1	3 hr at 600°C in argon	Khaki powder	NpO_2
10	Product of 4	3 hr at 600°C in argon	Shiny black particles	NpO_2
11	Product of 9	1 hr at 1000°C in air	Khaki powder	NpO_2
12	Product of 11	1 hr at 600°C in H_2	Khaki powder	NpO_2

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FIG. 1—X-ray patterns of U_3O_8 and Np_3O_8.

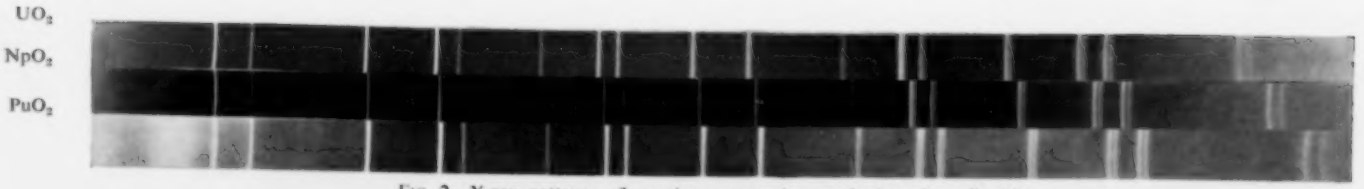

FIG. 2—X-ray patterns of uranium, neptunium and plutonium dioxides.

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TABLE 2.—X-RAY DATA FOR Np_2O_5

Miller indices	*d* value (Å)		Relative intensity
	calculated	observed	
001	4·16	4·14	100
110	3·45	3·45	90
200	3·27	3·27	55
111	2·65	2·66	80
201	2·56	2·58	60
002	2·08	2·09	70
020	2·03	2·04	50
301	1·92	1·93	50
021	1·83	1·83	50
112	1·78	1·79	75
202	1·75	1·76	50
–	–	1·75	50
220	1·72	1·73	50
–	–	1·65	30
221	1·59	1·60	60
401	1·53	1·53	30
–	–	1·50	20
022	1·45	1·46	50
122	1·42	1·42	55
321,033	1·40	1·39	55
130,222	1·33	1·33	60
113	1·28	1·29	60
420	1·28	1·28	50
131	1·26	1·27	40
421	1·22	1·22	30
231	1·20	1·20	30
–	–	1·16	30
123	1·13	1·13	30
132	1·12	1·12	20

There are 17 further lines in the region 1·12–0·837 Å

The lattice constant of NpO_2 calculated from the X-ray pattern was $a = 5{\cdot}4223 \pm 0{\cdot}0002$ kX and the calculated density was 11·14 g/cm³. The khaki and the black form gave identical X-ray patterns and derived cell dimensions.

Acknowledgement—The X-ray examinations were made by Dr. J. F. WALKER and Mr. B. J. MCDONALD.

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A simple preparation of Pu(VI) sulphate solutions

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ALTHOUGH ozone oxidizes Pu(IV) quantitatively to Pu(VI) in nitric and hydrochloric acids,[1] there appears to be some doubt regarding the oxidation in sulphuric acid. It has been reported that a

[1] H. W. MILLER and R. J. BROUNS *Analyt. Chem.* **24,** 536 (1952).

high percentage conversion of Pu(IV) to Pu(VI) by ozonization at tracer concentrations in dilute sulphuric acid is realized only in the presence of catalysts such as silver or cerous ions.[2] The presence of catalytic species in the resulting Pu(VI) solution is undesirable, and necessitates chemical separation, thereby eliminating the main advantage of a gaseous oxidizing agent. For this reason it appeared desirable to investigate the possibility of the complete oxidation of macro-concentrations of Pu(IV) by ozonization in the absence of catalysts.

EXPERIMENTAL DETAILS

A stock solution of Pu(IV) sulphate was prepared by dissolution of metallic plutonium in 3 M sulphuric acid, followed by filtration to remove any plutonium dioxide or undissolved metal, and

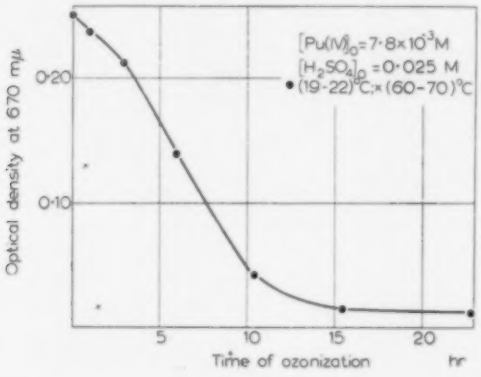

FIG. 1

evaporation to dryness. The solid was repeatedly evaporated to dryness with 98 per cent sulphuric acid to ensure that the plutonium was wholly in the tetravalent state. The Pu(IV) sulphate was weighed, dissolved in 0·25 M sulphuric acid and filtered again. The plutonium concentration was determined by weighing the plutonium dioxide obtained by ignition of aliquots at 1000°C. The Pu(IV) solution for ozonization was prepared by dilution of the stock solution.

At the flow rate used in the experiments the ozonized gas stream contained about 2 per cent ozone.

After various periods of ozonization aliquots of the plutonium solutions were withdrawn for optical examination in a Unicam SP 500 spectrophotometer. Optical densities were measured at room temperature in a 1 cm optical cell.

RESULTS

The course of the ozonization is most conveniently followed by observing the change in optical density at 670 mμ, since at this wavelength Pu(IV) absorbs appreciably while Pu(VI) exhibits a negligible absorption.[3] From Fig. 1 it is seen that the optical density reaches a limiting value of about 0·013 after 15 hr ozonization at 19–22°C. Assuming that the molar extinction coefficient of Pu(VI) at 670 mμ in dilute sulphuric acid is the same as in 1 M perchloric acid, i.e. $\simeq 2$,[3] then the optical density to be expected for complete conversion of Pu(IV) to Pu(VI) is $\simeq$0·016, in agreement with the observed value.

To confirm that the oxidation is complete, two aliquots of the Pu(IV) solution were oxidized, one with ammonium persulphate in the presence of a silver sulphate catalyst,[4] the other with ozone. In the latter case, the ozonized solution was made up to its original volume with water to compensate for solvent loss due to evaporation. The optical densities at 832 mμ (λ max.) were 1·035 and 1·045 for the persulphate and ozone oxidations respectively. Thus it is clear that ozone converts Pu(IV) quantitatively to Pu(VI). A slight increase in the optical density at 832 mμ to a value of 1·06, for

[2] G. T. SEABORG and J. J. KATZ *Actinide Elements, National Nuclear Energy Series* Div. IV, Vol. 14a, p. 277. McGraw-Hill, New York (1954).
[3] *Ibid.* Chap. 9.
[4] *Ibid.* p. 288.

the persulphate-oxidized solution after standing for a few days, is thought to be due to increased complexing of the Pu(VI) ion by sulphate ions generated by the slow silver ion-catalysed decomposition of the persulphate ion.[5]

Qualitative studies have shown that the oxidation of Pu(IV) by ozone in dilute nitric and perchloric acids proceeds at a much faster rate than in dilute sulphuric acid. The slow oxidation in the latter acid is presumably due to the increased stabilization of Pu(IV) by sulphate complexing. Complete oxidation of the Pu(IV) sulphate solution can be achieved in about 1½ hr by carrying out the ozonization at ≃65°C (Fig. 1).

In conclusion it should be pointed out that quantitative oxidation by ozone may be limited to fairly dilute sulphuric acid solutions, owing to reduction of Pu(VI) by water at high sulphuric acid concentrations.[6]

Acknowledgements—The author would like to express his appreciation of the assistance rendered by Messrs. D. E. GLANVILLE and F. DERRICK.

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[5] J. W. MELLOR *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. 10, p. 469. Longmans Green, London (1930).
[6] D. W. GRANT and D. E. GLANVILLE Unpublished work.

Study of the complex formation between silver ion and thiosulphate by the solubility method: Calculation of the composition of complexes in the system: $AgBr$–$Na_2S_2O_3$–H_2O

(*Received* 26 *September* 1957)

THE process of fixation of photographic negatives involves the dissolution of silver halides in sodium thiosulphate solution. The study of the reaction between silver and thiosulphate ions has received considerable attention, but the results of various workers like RICHARDS and FABER,[1] SCHWICKER,[2] LUTHER,[3] SCHMIDT,[4] ROSENHEIM *et al.*,[5] BAINES,[6] SPACU and MURGULESCU[7] and others, who isolated and analysed the complexes, are widely divergent, probably because the isolation of the pure product is beset with difficulties. Among the methods for the preparation of argentothiosulphate complexes are (i) saturating a solution of sodium thiosulphate with silver carbonate or chloride and (ii) adding ammoniacal silver nitrate to sodium thiosulphate and evaporating over sulphuric acid.

In publications from this laboratory, DEY and MUSHRAN[8] obtained a product having the composition $Ag_2S_2O_3,4Na_2S_2O_3,2H_2O$, by alcoholic precipitation of the compound from solutions of silver halide in sodium thiosulphate solution. They determined the valency of the complex anion by coagulation experiments and concluded that their product was contaminated with an excess of thiosulphate. DEY and BHATTACHARYA[9] observed that a precipitate of silver thiosulphate in presence of water was transformed to silver sulphide and they utilized this observation for the determination of thiosulphate in aqueous solution.

[1] T. W. RICHARDS and H. B. FABER *Amer. chem. J.* **21**, 167 (1899).
[2] A. SCHWICKER *Ber.* **22**, 1763 (1899).
[3] R. LUTHER *Photogr. Ind., Berl.* **26**, 626 (1928).
[4] R. SCHMIDT *Földt. Közl.* **23**, 38, 100 (1893).
[5] A. ROSENHEIM and S. STEINHAUSER *Z. anorg. chem.* **25**, 74 (1900); A. ROSENHEIM and F. TRWENDT *Ber.* **61**, 1731 (1928).
[6] H. BAINES *Photogr. J.* **53**, 314 (1929); *J. chem. Soc.* 2763 (1929).
[7] G. SPACU and J. G. MURGULESCU *Z. anorg. Chem.* **208**, 157 (1932).
[8] A. K. DEY and S. P. MUSHRAN *Proc. nat. Acad. Sci., India* **16A**, 37 (1947).
[9] A. K. DEY and A. K. BHATTACHARYA *J. Indian chem. Soc.* **23**, 124 (1946).

In further communications DEY advanced a new method for the calculation of the composition of complexes from solubility data. His calculations have successfully been applied to the systems: potassium halide—halogen,[10] silver chloride—sodium thiosulphate[11] and other complex forming systems.[12]

In this report the dissolution of silver bromide in sodium thiosulphate solutions has been studied at different temperatures, and the compositions of the complex ions formed have been calculated with the help of similar expressions. The reaction between silver ion and thiosulphate may be represented by:

$$n\mathrm{Ag}^{+} + \mathrm{S_2O_3}^{--} \rightleftharpoons [\mathrm{Ag}_n\mathrm{S_2O_3}]^{-(2-n)}$$

If a_1 and a_2 are the concentrations of silver dissolved in c_1 and c_2 concentrations of thiosulphate respectively, the value of n works out as:

$$n = \frac{-\left(\log\frac{a_1}{a_2} - \log\frac{c_1}{c_2}\right) \pm \sqrt{\left(\log\frac{a_1}{a_2} - \log\frac{c_1}{c_2}\right)^2 - \left(4\log\frac{a_1}{a_2}\left(\frac{a_1}{c_1} - \frac{a_2}{c_2}\right)\right)}}{2\log a_1/a_2}$$

This expression can be used to calculate the stoicheiometry of the complexes formed in solution.

EXPERIMENTAL

Standard solutions of silver nitrate and of sodium thiosulphate were prepared and standardized by the usual methods. All reagents used were of analytical grade. 10 ml of 0·25 M silver nitrate were taken in different test tubes and silver bromide was precipitated by the addition of sodium bromide solution. The precipitates were washed as usual, and transferred quantitatively to filter paper cones in funnels. The filter paper was then punctured at the apex with a pointed glass rod and the precipitate received in 100 ml measuring flasks with the help of a jet of water from a wash bottle. Any precipitate that remained adhering to the filter was also considered as will be seen later. A measured volume* of decinormal sodium thiosulphate was added to each flask and the volumes raised to 100 ml. The flasks were shaken for 1 hr in a mechanical shaker and kept in a thermostat for 4 hr with occasional shaking. The undissolved precipitates were then filtered using funnels jacketted with water at the temperature of the thermostat. The undissolved silver bromide was filtered and washed thoroughly. The filter with the precipitate along with the corresponding punctured filter paper was then treated for the estimation of silver. Knowing the amount of silver bromide taken initially and that remaining undissolved, the amount of silver bromide dissolved in a particular concentration of thiosulphate was known.

The solubility of silver bromide in various concentrations of sodium thiosulphate was determined at different temperatures, and the value of n determined with the help of the expression derived. The results are given below:

TABLE 1.—TEMPERATURE = 30°C

Final concentration of $Na_2S_2O_3$	AgBr dissolved (g atoms of Ag)	Value of n
0·08 M	0·000551	—
0·07	0·000505	0·51
0·06	0·000456	0·51
0·05	0·000404	0·51
0·04	0·000349	0·51
0·03	0·000287	0·47
0·02	0·000254	0·43

* The volume of sodium thiosulphate solution was so chosen as to effect incomplete dissolution of the precipitated silver bromide.

[10] A. K. DEY *J. Indian chem. Soc.* **24**, 207 (1947); *Proc. nat. Acad. Sci., India* **25A**, 202 (1956).
[11] A. K. DEY *Proc. nat. Acad. Sci., India* **25A**, 205 (1956).
[12] A. K. DEY *Dokl. Akad. Nauk U.S.S.R.* **58**, 1047 (1947).

TABLE 2.—TEMPERATURE = 50°C

Final concentration of $Na_2S_2O_3$	AgBr dissolved (g atoms of Ag)	Value of n
0·08 M	0·000650	—
0·07	0·000600	0·67
0·06	0·000546	0·63
0·05	0·000488	0·62
0·04	0·000425	0·61
0·03	0·000355	0·60
0·02	0·000275	0·59
0·01	0·000175	0·53

TABLE 3.—TEMPERATURE = 75°C

Final concentration of $Na_2S_2O_3$	AgBr dissolved (g atoms of Ag)	Value of n
0·08 M	0·000720	—
0·07	0·000672	0·94
0·06	0·000620	0·91
0·05	0·000562	0·86
0·04	0·000498	0·84
0·03	0·000425	0·82
0·02	0·000339	0·79
0·01	0·000228	0·74

From the results above we find that at a temperature of 30°C, the value of n is about 0·5, showing that the complex anion in solution is $[Ag(S_2O_3)_2]^{---}$, while at 75°C n is more nearly equal to unity, corresponding to $[Ag(S_2O_3)]^-$. At 50°C, the value of n lies between unity and 0·5, showing that both species are present in solution. The relative amounts of the two ions also appear to depend upon the concentration of thiosulphate solution.

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The anion-exchange separation of iodine anions

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We should like to report a method for separating iodide-iodate mixtures and iodide-periodate mixtures where either "tracer" concentrations or milligram quantities of the anions are present.

The separation was accomplished using an ion-exchange column, 12 mm in diameter, packed to a height of 50 cm with Amberlite IRA-400 (OH^- form) resin, mesh size, 20-50. The column was

pretreated by converting the resin to the nitrate form with 1 M nitric acid; washing with distilled water until the eluant was neutral and bringing the liquid associated with the column to a pH of 10·5 by washing with dilute sodium hydroxide. The samples of I^{131} tagged anions (all solutions adjusted to a pH of 10·5) were placed on the column and eluted with 200 ml of dilute sodium hydroxide solution at a pH of 10·5 followed by 1000 ml of 1 M potassium nitrate at a pH of 10·5. The eluant was fed into the column by gravity flow from a 1000-ml separatory funnel. After passing through the column, the eluant was channelled into a glass envelope surrounding a Geiger tube. The Geiger tube was connected to a Brown recorder through a count-rate meter so that continuous monitoring of the I^{131} in the eluant could be done. The exit from the Geiger-tube envelope led to a capillary tube which expelled the eluant at a height even with the top of the column. The flow-rate was adjusted to approximately 3 ml per min, which means that the exchange system was probably not at equilbrium. However, the results obtained were not altered appreciably if the flow-rate was decreased to 0·5 ml per min.

The tagged anion samples were made by first adding excess carrier iodide to an Oak Ridge solution of I^{131} (the chemical form of the active iodine being iodide). The resulting active-iodide solution was then oxidized to iodate with excess potassium chlorate and subsequently to periodate with chlorine in alkaline solution.*

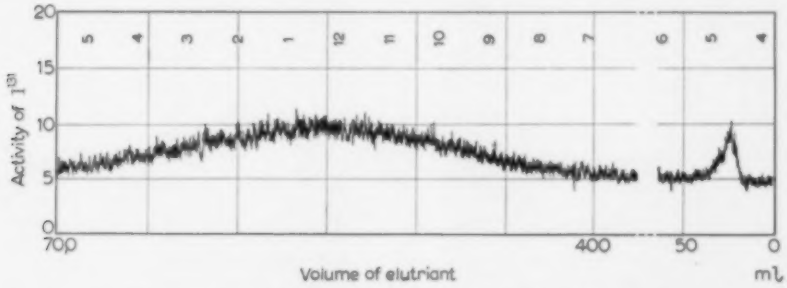

FIG. 1.—Chromatographic chart of stock I^{131} solution, showing IO_3^- and I^- peaks.

To obtain the exchange characteristics of the individual anions, samples containing only a single anion were placed on the column. The chromatograph from the Brown recorder was actually a plot of time versus counts per minute of I^{131}. However, since the flow-rate was kept constant and the activity was proportional to the anion in question, the chromatograph could be assumed to be a plot of concentration of anion versus volume of eluant. For iodide samples, a broad activity peak extended from 300 ml to 1000 ml of 1 M potassium nitrate eluant. The iodide in the eluant was precipitated with silver nitrate, and better than 95% recovery was obtained. A sharp elution peak between 25 and 70 ml of 1 M potassium nitrate was obtained for both the iodate and periodate samples. The per cent recovery of the iodate was determined by treating the 50 ml of eluant associated with the activity with excess iodide in acid solution, and titrating the liberated iodine with thiosulphate solution. Again better than 95% recovery of the anion was obtained. Some of the solution was made just basic and treated with excess iodide to prove that the anion in the eluant was not periodate. No iodine was liberated, so the active material must have all been in the form of iodate. Periodate was analysed for by making the eluant just basic, adding excess iodide, and titrating the liberated iodine with arsenious acid. 95% recovery was obtained.

Iodate-iodide mixtures and periodate-iodide mixtures were put on the column and eluted as done previously. The eluant corresponding to each peak was analysed as above. Complete separation and 95% recovery of each anion was obtained.

More samples of the various anions were made as described above, except no carrier iodine was added. Here, since all of the iodine present was supposedly I^{131}, the per cent recovery was calculated by comparing the counting rates of aliquots of the original samples and aliquots of the eluant. Identity of the anions in the sample and in the eluant was established by shaking the solutions with 0·01 M iodine in carbon tetrachloride and determining the amount of activity which exchanged.

* H. S. BOOTH (Editor) *Inorganic Synthesis* Vol. 1, pp. 168-171. McGraw-Hill, New York, N.Y. (1939).

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Iodide exchanges readily with iodine, while iodate and periodate do not exchange appreciably. Again the exchange characteristics and the per cent recovery of each anion was similar to that found for macro concentrations.

Fig. 1 is a typical chromatograph of the separation of iodide from iodate at tracer concentrations. Similar chromatographs were obtained for iodide-periodate mixtures. If the flow-rate is kept constant, the percentage of each anion can be found by determining the area under each peak with a planimeter and relating this to the total area. This is a useful tool where only the ratio of oxidized to reduced iodine in tracer solutions is desired.

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NOTE TO AUTHORS

WHEN authors submit papers describing investigations in which X-ray powder measurements were made, but omitting the actual X-ray data, it is requested that these data be submitted to the Editor of the Joint Committee on Chemical Analysis by powder diffraction methods for possible inclusion in the "X-ray Powder Data File," published by the A.S.T.M.

The data should contain accurate listings of d values and intensities of reflections. Other items of information of value for the data file are: hkl indices and lattice parameters if known, radiation used, type of X-ray recording employed, method of estimating intensities (visual, photometric, Geiger-counter), plus any relevant information concerning the nature and preparation of specimens studied.

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BOOK REVIEW

E. CARTMELL and G. W. A. FOWLES: **Valency and Molecular Structure.** London: Butterworths Scientific Publications, 1956. 256 + xi pages. 32s. 6d.

THIS is a book providing an introductory account of modern theories on the nature of the chemical bond and describing some of their applications to molecular structures. Sufficient mathematics is included to provide the reader with an insight into the wave-mechanical basis of the theories. The book usefully bridges the gap between advanced works on the subject and elementary non-mathematical accounts, which do not provide sufficient intellectual satisfaction for the serious student of chemistry. It is intended primarily for first year honours students, although parts are suitable for more advanced courses. In addition, it may be strongly recommended to the attention of practising chemists, who for some reason may not be very familiar with the modern ideas on valency.

The book is in three parts. Part I deals with the origin and development of the quantum theory and its application to atomic structure. It includes a brief outline of the solution of the Schrödinger equation for the hydrogen atom and indicates how the wave equation leads to the directional characteristics of atomic orbitals. Part II discusses the quantum theory of valency. The valency-bond method together with the theory of resonance, the molecular-orbital method, and the question of directed valency, are all treated in a simple lucid manner. Part III describes the application of these approaches to a series of inorganic compounds, and discusses briefly features such as the electronegativity concept, and the hydrogen bond. The selection of compounds treated is well made, and includes complex compounds (including sandwich complexes) and electron-deficient substances.

In writing a book of this type, it cannot be easy in all cases to decide upon the exact order and extent of treatment of the different topics to be discussed. In the present case the general arrangement is excellent. It might have been preferable, however, not to have introduced the electronegativity concept in a chapter entitled "Bonding in Solid Structures," since PAULING's most reliable electronegativity values have been obtained using the bond energies of gaseous substances. Also, in this connection, in the light of the studies of ROBINSON, RITTNER, TOWNES and DAILEY, and others, the inclusion of the empirical equation of HANNAY and SMYTH, and of Figure 51, seems to be unjustified.

Each chapter in the book has a list of references at the end, and these seem to have been carefully chosen. The printing of the text and the reproduction of the many diagrams are excellent; the "printer's errors" appear to be relatively few in number, one being at the bottom of page 10, which should read $1\,cm^{-1} = 2{\cdot}8575$ cal $mole^{-1} = 1{\cdot}23954 \times 10^{-4}$ eV $atom^{-1} = 1{\cdot}9858 \times 10^{-16}$ ergs.

The authors are to be congratulated on this book, which they emphasize is written by chemists for chemists.

D. F. C. MORRIS

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 77 to 90. Pergamon Press Ltd., London

MASS SPECTRA OF HALOGEN FLUORIDES*

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(*Received* 16 *May* 1957)

Abstract—Appearance potentials and positive-ion mass spectra were determined for IF_5, BrF_5, BrF_3 and ClF_3. A negative-ion study was made on BrF_3. The gas samples were subjected to rate of effusion studies in the mass spectrometer sample system and shown to contain diatomic halogen and halogen fluoride impurities. Halogen oxyfluorides were detected in BrF_5, BrF_3 and ClF_3 samples and reaction between O_2 and BrF_5 was observed on mixing. Upper limits for ionization potentials were obtained for IF_5, IF, ICl, IBr, BrF_2, BrF, BrCl, ClF_2 and ClF directly from appearance potentials. Ionization potentials for the radicals BrF_2 and ClF_2 were deduced using supplementary thermochemical data. Ionization potentials of diatomic interhalogens with the exception of BrCl give bond dissociation energies for interhalogen molecule ions approximately equal to corresponding values for neutral molecules.

THE literature contains many unsettled questions concerning the existence and properties of some halogen fluorides and their derivatives. Polyatomic halogen fluorides are extremely reactive and frequently suspected of containing lower molecular weight halogen and halogen fluoride impurities in spite of diligent attempts at purification. A mass spectrometer study of these compounds was initiated to determine mechanisms of electron impact reactions, ionization potentials and the state of purity of samples of ClF_3, BrF_3, BrF_5 and IF_5.

EXPERIMENTAL

A Consolidated Engineering Corp. 21-120 mass spectrometer was used to obtain mass spectra and appearance potentials. This spectrometer differed from the conventional 180°, 5 in. radius, 21-103, in that it was equipped with an aluminium block sample system and an aluminium foil leak. Subsequent experiments were carried out using a monel sample system consisting of two 1 l. welded monel cans serving as sample reservoir chambers and an appropriate manifold made from monel tubing and monel swagelock fittings. The swagelock fittings were eventually replaced by welds to eliminate the possibility of leaks. The valves used were Hoke No. 1228 valves constructed of monel with Teflon seats. This monel system was enclosed in an asbestos box fitted with strip heaters, so that conditioning and operation at temperatures as high as 100°C was possible. The temperature limit was determined by the stability of Teflon gaskets and valve seats. Reservoirs were fitted with Imperial Red Top valves for rapid evacuation. These valves were brass and had to be nickel-plated prior to use with the halogen fluorides.

The pumping system used for the sample manifold consisted of a Distillation Products M.H.G. 50·02 stainless-steel mercury diffusion pump and a Welch Duo Seal mechanical pump to maintain the fore vacuum. Rough pumping of the system for

* Research performed under the auspices of the U.S. Atomic Energy Commission.

larger quantities of halogen fluorides was done with a Welch pump filled with Kel-F oil. Both pumps were vented to the outside atmosphere.

DISCUSSION OF RESULTS

Composition of gases

Mass spectra of purified samples of BrF_3, BrF_5, ClF_3 and IF_5 are presented in Table 1. These spectra were taken after several days of conditioning of the inner surface of the aluminium sample system by exposure to relatively high pressures of BrF_3. Prior to this treatment of the sample system, spectra consisted mainly of Br^+ and

TABLE 1.—MONOISOTOPIC MASS SPECTRA OF SOME HALOGEN FLUORIDES (50 V ELECTRONS)

M/e	IF_5		*M/e*	BrF_5	
254	I_2^+	1686	174	BrF_5^+	—
222	IF_5^+	100·0	158	Br_2^+	11·7
203	IF_4^+	976	155	BrF_4^+	100·0
184	IF_3^+	189	136	BrF_3^+	26·4
165	IF_2^+	70·1	133	$BrOF_2^+$	0·5
146	IF^+	97·6	117	BrF_2^+	38·5
127	I^+	514	114	$BrOF^+$	1·6
			111	BrO_2^+	0·4
			98	BrF^+	18·8
			95	BrO^+	0·8
			79	Br^+	17·4

M/e	ClF_3		*M/e*	BrF_3			
92	ClF_3^+	100·0	158	Br_2^+	48·7		
73	ClF_2^+	985	136	BrF_2^+	100·0		
70	$ClOF^+$, Cl_2^+	57·2	133	$BrOF_2^+$	3·6		
			130	BrO_2F^+	6·6		
67	ClO_2^+	18·3	117	BrF_2^+	144	BrF_2^-	1·9
54	ClF^+	647	114	$BrOF^+$	13·2		
51	ClO^+	44·7	111	BrO_2^+	8·9		
35	Cl^+	11·3	98	BrF^+	202		
			95	BrO^+	9·4		
			79	Br^+	26·6	Br^-	1·5
			38			F_2^-	0·6
			19			F^-	4·7

Br_2^+ ions with a large number of unidentified low-intensity ions. Even after conditioning the spectrometer sample system and reproducible mass spectra of a given halogen fluoride were obtained, introduction of other species showed evidence of surface reactions. For example, BrF_3 samples run after IF_5 samples would give IBr peaks that gradually disappeared on flushing the sample system with more BrF_3. The converse effect of IF_5 reacting with a surface coated with bromine fluoride compounds was not observed.

Having demonstrated the importance of surface reactions and noting further that all spectra contain evidence for homonuclear diatomic halogen ions,* one considers to what extent the spectra observed represent gases admitted to the sample manifold.

The following procedure was used to determine the purity of gas flowing from the spectrometer sample system into the ion source. The gas reservoir was filled to a convenient operating pressure and spectra were taken at periodic time intervals as the sample was pumped out through the leak. If the reservoir contained a pure gas, then ions formed from it should fall on parallel lines when the log relative ion intensity is plotted against time. If a mixture of gases is produced by reaction in the sample system or the gas initially introduced consists of more than one component, then

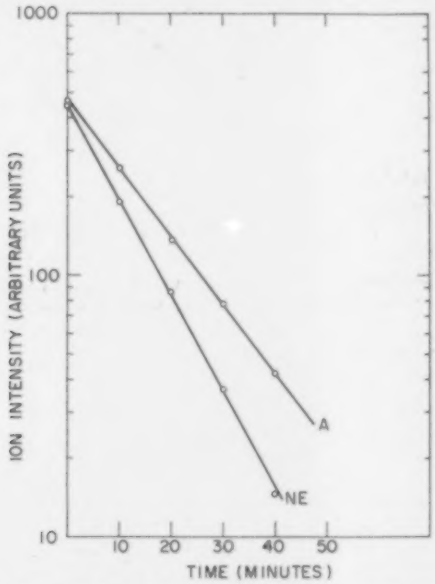

FIG. 1.—Rate of effusion of A and Ne (aluminium sample system; 50 V electrons).

fractionation of the mixture should occur during the effusion process and plots of log peak intensity vs. time may have different slopes, indicating a multicomponent system. The spectrometer sample system is designed for operating conditions that approximate ideal gaseous effusion for permanent gases, so that relative flow rates should vary inversely with the square roots of the molecular weights of respective molecules in the sample system. Consequently, if flow rates do not follow this law, one may conclude that the rate-determining step in flow is controlled by processes other than collisions of molecules with the leak. Such processes may be desorption of molecules from the reservoir or reaction either at the surface of the sample system or in the gas.

Figs. 1–5 show leak-rate data for the halogen fluorides and a mixture of neon and argon, all taken with the aluminium sample manifold. The rare-gas study in Fig. 1 confirmed conditions of ideal-gas effusion assumed for the sample reservoir and leak. The BrF_3 run in Fig. 2 shows growth of Br_2, indicating a chemical reaction, and a different effusion rate for parent molecules giving BrF^+ and BrF_3^+. BrF_2^+ is apparently

* Cl_2 in ClF_3 is interfered with somewhat by ClOF, but its presence is fairly certain from isotope abundance measurements in this mass region.

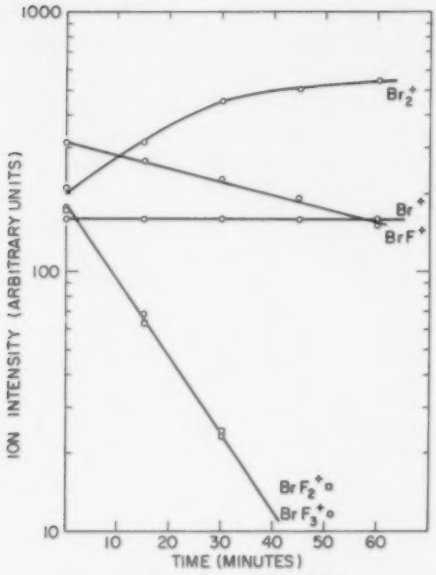

FIG. 2.—Rate of effusion of BrF_3 (aluminium sample system; 50 V electrons).

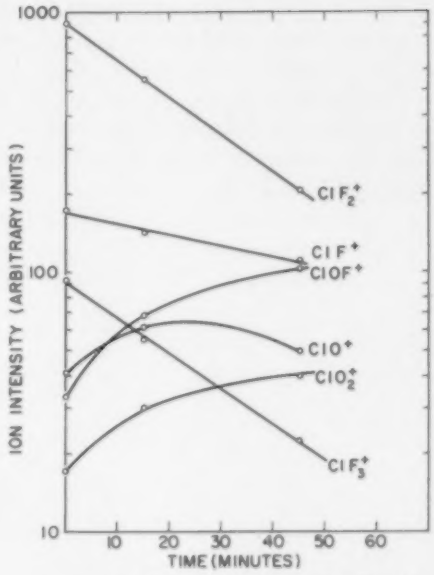

FIG. 3.—Rates of effusion of ClF_3 and chlorine oxyfluorides (aluminium sample system; 50 V electrons).

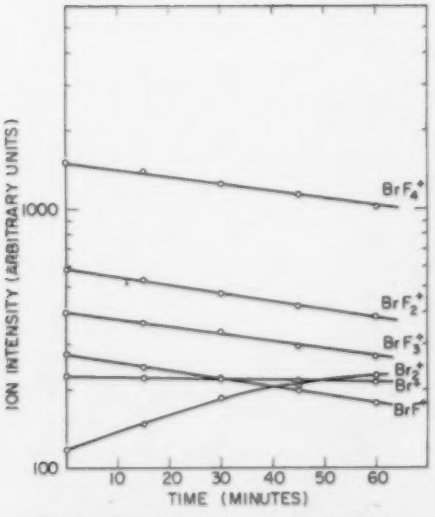

FIG. 4.—Rate of effusion of BrF_5 (aluminium sample system; 50 V electrons).

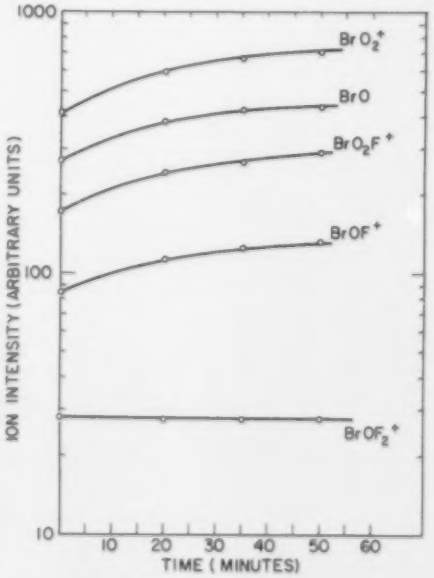

FIG. 5.—Rate of effusion of bromine oxyfluoride formed by direct reaction of O_2 and BrF_5 (aluminium sample system; 50 V electrons).

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formed from the same molecule that produces BrF_3^+. The lower effusion rate of molecules giving BrF^+ eliminates the simple mechanism of two different gases flowing into the ionization chamber. There is the possibility that the rate-determining step in the flow process is either a reaction producing BrF or slow desorption of BrF from the aluminium fluoride-covered walls. The hypothesis of a rate-controlling reaction is unlikely in view of the fact that it would very probably involve BrF_3 as a reactant and considerable BrF^+ is still obtained after all the BrF_3^+ has been pumped out. The Br^+ ion intensity shows practically no change with time over a 60 min period.

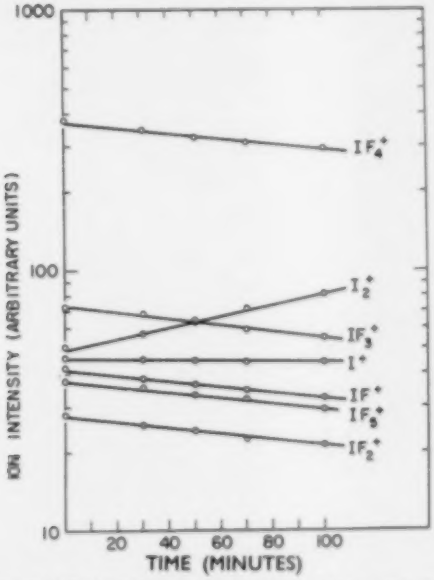

FIG. 6.—Rate of effusion of IF_5 (aluminium sample system; 50 V electrons).

This proves that very little of it is formed from BrF_3 and that it must be formed in roughly equal proportions from Br_2 and BrF.

The plot of effusion data for ClF_3 in Fig. 3 is very similar to the BrF_3 data. Growth of $ClOF^+$ with time gives evidence for formation of oxyfluorides in the sample system. We note again that ClOF and Cl_2 containing ^{35}Cl are unresolved in these experiments.

The plot of effusion rates for BrF_5 ions, Fig. 4, shows a growth of Br_2^+ and a flat Br^+ line similar to plots for these ions in BrF_3. The bromine fluoride ions all fall on parallel lines. This is consistent with formation from a unique parent molecule, BrF_5. The flat Br^+ line again establishes two sources of Br_2^+. Since the Br_2^+ in the BrF_5 spectrum is considerably weaker than in BrF_3, a small contribution of Br^+ from BrF_5 would easily produce the observed effect. The absence of appreciable quantities of BrF^+ in BrF_5 is consistent with the relatively small Br_2^+ peak. Detection of very small amounts of BrF in BrF_5 will be considered in subsequent discussions of appearance potentials and ionization efficiency curves.

A rather interesting feature of both BrF_3 and BrF_5 spectra is the observation of bromine oxide and bromine oxyfluoride ions. RUFF and MENZEL[1] suspected the

[1] O. RUFF and A. MENZEL *Z. anorg. Chem.* **183**, 214 (1929).

synthesis of $BrOF_3$ from the reaction of BrF_5 with water, but this molecule has never been isolated and there has been considerable doubt as to its existence. A mixture of O_2 and BrF_5 was run to see if reactions producing oxyfluorides took place in the sample system. The O_2 was admitted to the spectrometer first and a 20 per cent drop in the O_2^+ ion was observed on introduction of BrF_5 to the sample system. The growth rates of bromine oxyfluoride ions are shown in Fig. 5. The curves show at least two species present probably $BrOF_3$ and BrO_2F. The latter is formed more rapidly than the former under these conditions. Similar studies showed a reaction of Br_2 and BrF_3

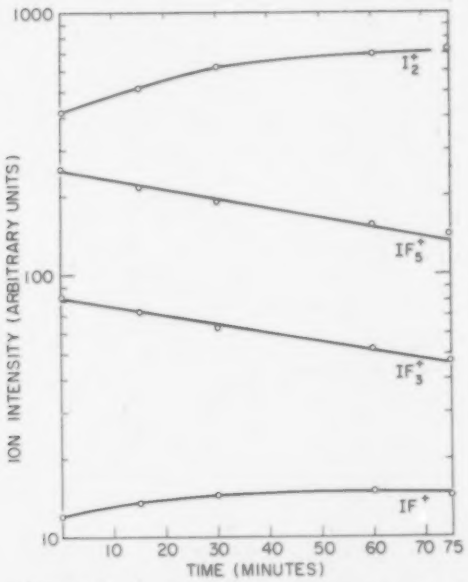

Fig. 7.—Rate of effusion of IF_5 (aluminium sample system; 19 V electrons).

producing BrF, but no reaction of Br_2 with BrF_5. Attempts to measure equilibria of Br_2 and BrF_3 failed because of inability to quantitatively reproduce surface conditions.

Figs. 6 and 7 show rate of effusion data for IF_5 taken at the usual 50 V electron accelerating potential and at 19 V. The data taken with 50 V electrons are similar to BrF_5, showing a family of parallel lines for iodine fluoride species, a flat line for I^+ and growth for I_2^+. The 19 V data were taken to eliminate the contribution of IF^+ formed from IF_5 on the assumption that it would not be produced at this low voltage. IF_5^+ and IF_3^+ still fall on parallel lines, but now IF^+ clearly shows a growth similar to I_2^+. This is good evidence for the existence of IF under conditions of room temperature and at pressures of the order of 0·1 mm Hg in the mass spectrometer sample system. It was not possible to critically test for the presence of IF_3 because of the much smaller difference between the estimated appearance potential of IF_3 from IF_5 and ionization potentials of IF_3. IF_5 proved to be the most inert of the halogen fluorides studied in this work. No reaction with O_2 was detected at room temperature and up to 100°C. Br_2 reacted with IF_5 on contact in the aluminium sample manifold, giving IBr and no detectable yield of BrF_3.

The lower fluorides of iodine are of considerable interest, and failure to detect

them outside of flame spectra has led DURIE and GAYDON[2] to postulate that IF was unstable because of a relatively low bond dissociation energy, 1·98 eV. This value was derived from spectroscopic data on the assumption that the products of dissociation are $I(^2P_{1/2})$ and $F(^2P_{3/2})$. The alternative $I(^2P_{3/2})$ and $F(^2P_{1/2})$ gives 2·87 eV for the bond energy. A similar choice exists for BrF with 2·16 eV and 2·64 eV as respective values for bond energies. ClF is considered as going to the $Cl(^2P_{3/2})$ and $F(^2P_{1/2})$ states with a

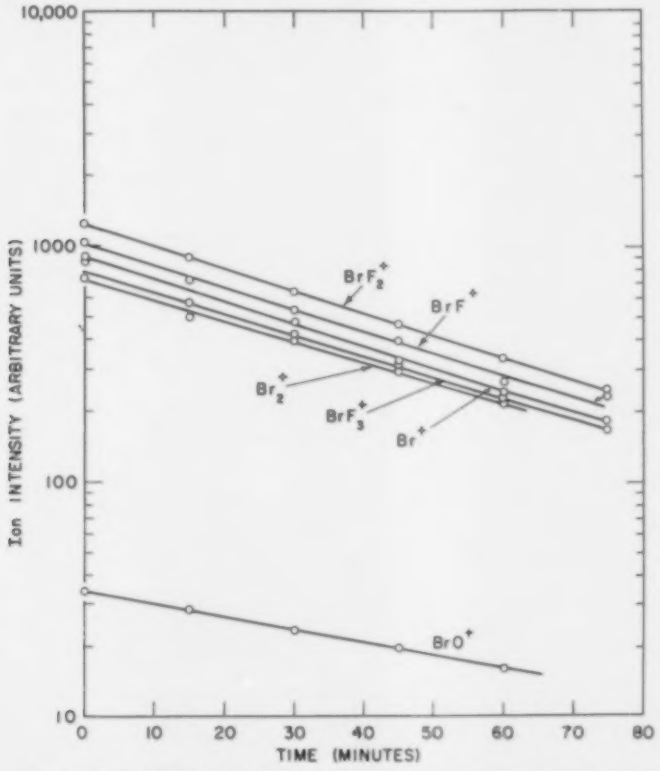

FIG. 8.—Rate of effusion of BrF_3 (cold monel sample system; 50 V electrons).

dissociation energy of 2·616 eV. SLUTSKY and BAUER[3] have computed minimum average bond energies for IF, BrF and ClF bonds in the polyatomic halogen fluorides and have concluded that their data support the higher bond energies. Detection of IF and BrF as relatively stable species in mass spectra helps eliminate one of the major features of DURIE and GAYDON's argument for lower bond energies.

The rate of effusion data presented above has been obtained with an aluminium system which interacted extensively with the samples. Rates of effusion for BrF_3 were taken from a monel system and are presented in Figs. 8 and 9. Here one notes, at room temperature, no growth of Br_2 and only a mild difference in slope between Br_2 and BrF_3. BrF^+ appears to be formed primarily from BrF_3 and the only ion showing an obviously different leak rate is the bromine oxide BrO^+. The system on heating to

[2] R. A. DURIE and A. G. GAYDON *J. phys. Chem.* **56**, 316 (1952).
[3] L. SLUTSKY and S. H. BAUER *J. Amer. chem. Soc.* **76**, 270 (1954).

approximately 100°C showed a difference in slopes of BrF^+ and BrF_3^+, indicating surface reactions on monel at higher temperatures. The monel system is apparently more inert or covered with a more stable fluoride film than the aluminium system. The reaction of Br_2 and BrF_3 giving BrF did not go at room temperature in monel. It is apparent that if one wishes to study physical properties of these compounds in the pure state, aluminium is completely unsatisfactory. It does provide a means of generating the diatomic halogen fluorides making possible a determination of their ionization potentials.

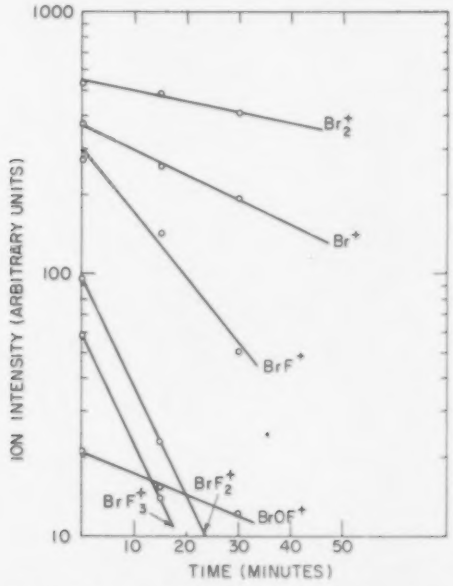

FIG. 9.—Rate of effusion of BrF_3 (hot monel sample system; 50 V electrons).

Appearance potentials and ionization mechanisms

Table 2 contains appearance potentials which set upper limits for the vertical ionization potentials of IF_5, IF, ICl, IBr, BrF_3, BrF, BrCl, ClF_3 and ClF. These appearance potentials were determined by the vanishing current method and the voltage scale was calibrated using the rare-gas ionization potentials. A trend of increasing ionization potentials with increasing F content is noted in the respective halogen fluoride systems, i.e. $BrF_3 > BrF$ and $ClF_3 > ClF$, etc.

Ionization efficiency curves for most species are typical of those obtained in electron impact studies where ions are formed by one mechanism or mechanisms having very similar energy requirements. Linear regions of these ionization efficiency curves showed no detectable "breaks" or changes in slope. In cases where changes of slope were detected, second values of appearance potentials are estimated and set in parentheses below the lower threshold. An example of this is the IF^+ ionization efficiency curve in Fig. 10. A second mechanism setting in at approximately 24 eV is quite obvious in this figure. Curves for Br^+, Cl^+, BrF^+ and IF_5^+ were similar, although the "break" in the curve for IF_5^+ was somewhat less well defined. IF_3^+, IF_2^+

and IF_4^+ curves are shown in Fig. 11. The IF_3^+ curve was carefully checked for evidence of IF_3 in IF_5, but no break in the linear portion was detected. However, the IF_3^+ and IF_2^+ ionization efficiency curves are quite different from the others in that they both show extremely long tails. This may be interpreted as evidence for very

TABLE 2.—APPEARANCE POTENTIALS OF SOME HALOGEN FLUORIDE AND INTERHALOGEN IONS
(All data in volts)

Halogen fluorides			
IF_5		BrF_5	
IF_5^+	13·5 ± 0·2 (~21·8)		
IF_4^+	13·6 ± 0·3	BrF_4^+	14·0 ± 0·3
IF_3^+	11·5 ± 0·3	BrF_3^+	15·5 ± 0·2
IF_2^+	15·1 ± 0·3	BrF_2^+	16·1 ± 0·2
IF^+	10·5 ± 0·3 (~24)	BrF^+	11·9 ± 0·3 (~20)
I^+	8·6 ± 0·2	Br^+	10·1 ± 0·3
ClF_3		BrF_3	
		Br_2^+	10·7 ± 0·3
ClF_3^+	13·0 ± 0·2	BrF_3^+	12·9 ± 0·3
ClF_2^+	12·8 ± 0·3	BrF_2^+	13·5 ± 0·3
ClF^+	12·7 ± 0·3	BrF^+	11·8 ± 0·2
		Br^+	10·3 ± 0·3 (~14)
Interhalogens			
$BrCl^+$	11·1 ± 0·2		
ICl^+	10·4 ± 0·2		
IBr^+	10·3 ± 0·2		

improbable processes with relatively low appearance potentials. Possibly IF_3 itself in trace quantities is responsible for these lower-energy reactions or the reactions

$$IF_5 \rightarrow IF_3^+ + F^- + F \quad (1)$$

or $$\rightarrow IF_3^+ + F_2^- \quad (2)$$

in competition with $$\rightarrow IF_3^+ + 2F \quad (3)$$

would produce this effect.

In order to deduce dissociation mechanisms for the decomposition of polyatomic halogen fluoride by electron impact, radical ionization potentials and bond dissociation

energies are needed. SLUTSKY and BAUER[3] have estimated minimum average bond energies for Br—F, Cl—F and I—F in polyatomic halogen fluorides, but unfortunately no data on ionization potentials of halogen fluoride radicals are available.

A further limitation on mechanism considerations comes from the X_2 and XF impurities which complicate the spectra in the region XF^+ and X^+ in all cases investigated. The only dissociation processes that may be considered in ClF_3 and BrF_3 with reliable appearance potential data are losses of F or F^-.

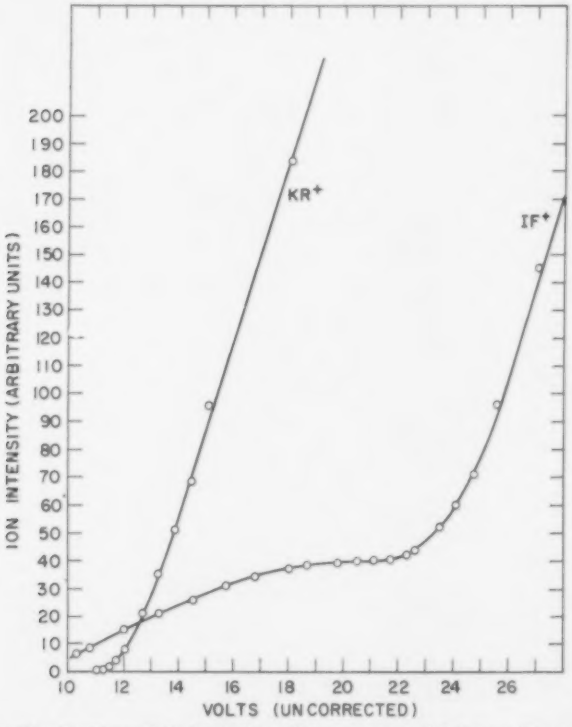

FIG. 10.—Portions of the ionization efficiency curve of IF^+ from IF_5 and of KR^+.

A negative-ion study on BrF_3 showed small relative yields of F^-, F_2^-, BrF_2^-, etc. The data are in Table 1 with the positive-ion mass spectrum of BrF_3. Since the collection efficiency of positive and negative ions from mass spectrometer ion sources is known to differ, the negative-ion spectrum was normalized on the reaction

$$Br_2 \rightarrow Br^+ + Br^- \qquad (4)$$

in the following way. The amount of Br^+ from Br_2 was determined independently. This, with the Br_2^+ observed in the BrF_3 spectrum, sets an upper limit for Br^-. This limit can be further reduced by inspection of the Br^+ ionization efficiency curve, Fig. 12. The two processes giving Br^+ differ by approximately 4 eV and are probably reaction (4) and the corresponding positive–negative ion reaction from BrF in the lower-energy region and reactions producing atoms of Br and F above 14 eV. If we assume that all of the reactions below 14 eV are (4), then an upper limit of the extent to which (4) contributes to Br^+ ions may be estimated. This gives a rough relative collection efficiency of

0·5 for negative–positive ions in this mass spectrometer. The relatively small fraction of total Br^+ via reaction (4) is consistent with results for Cl^+ and the general observation that cross-sections for production of negative ions are lower than for positive ions.

The ionization efficiency curve for F^- shown in Fig. 13 is similar to data obtained

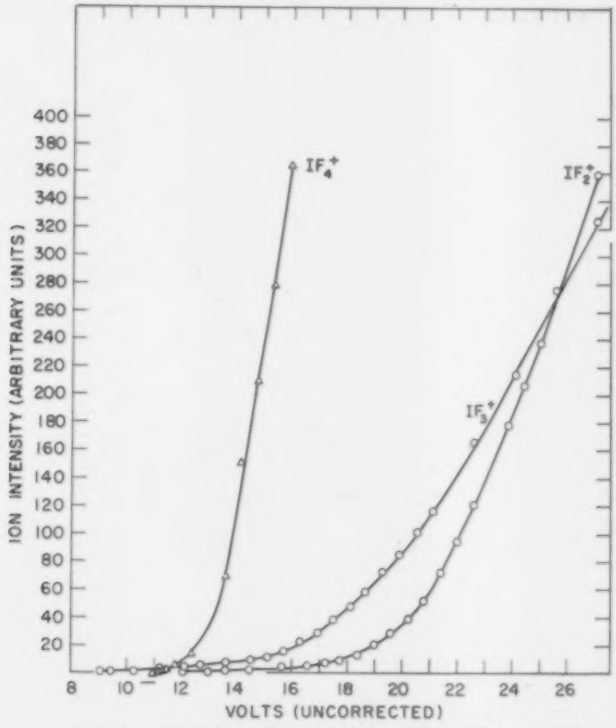

FIG. 11.—Ionization efficiency curves of IF_2^+, IF_3^+, and IF_4^+.

by AHEARN and HANNAY[4] for F^- from SF_6. There are two relatively intense resonance capture processes and one low-intensity peak that may be formed by positive-negative ion dissociation. This would give rise to a break in the ionization efficiency curve for BrF_2^+ from BrF_3 or a low-energy tail if it were formed by

$$BrF_3 \rightarrow BrF_2^+ + F^- \qquad (5)$$

The F^- may come from dissociation of BrF and possibly traces of HF and F_2 present in the sample. It is not present in sufficient quantity to perturb the BrF_2^+ ionization efficiency curve, so that dissociation of BrF_3 must be via reaction

$$BrF_3 \rightarrow BrF_2^+ + F \qquad (6)$$

The appearance potentials of BrF_2^+ and ClF_2^+ taken with appropriate bond dissociation energies for Br—F and Cl—F from SLUTSKY and BAUER[3] give ionization potentials of 11·2 and 11·0 eV for BrF_2 and ClF_2 respectively, assuming a reaction similar to (6) for ClF_2^+ formation.

[4] A. J. AHEARN and N. B. HANNAY *J. chem. Phys.* **21**, 119 (1953).

No evidence is available to choose between the reactions

$$BrF_5 \rightarrow BrF_4^+ + F \quad (7)$$

$$BrF_5 \rightarrow BrF_4^+ + F^- \quad (8)$$

for the production of BrF_4^+. Reaction (8) can be used to set an upper limit of 15·6 eV for the ionization potential of BrF_4. A value of 3·7 eV for the electron affinity of F

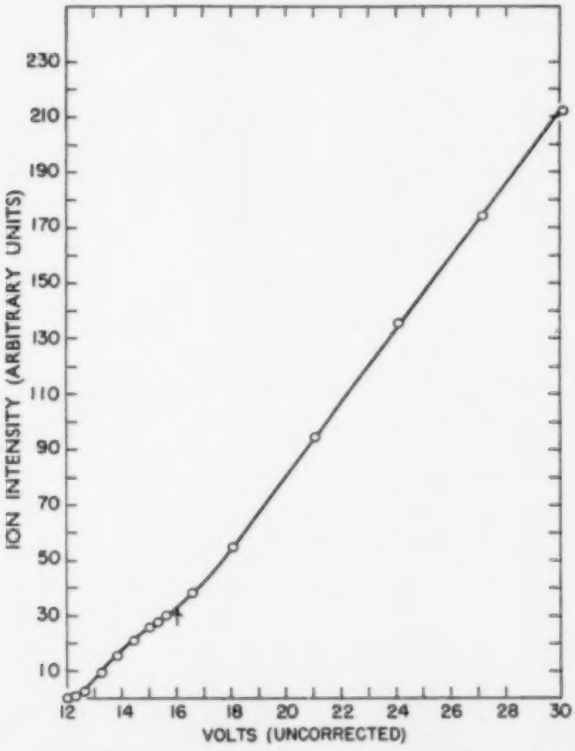

FIG. 12.—Appearance potential curve of Br^+ from BrF_3.

was used in this computation. This was based on 1·6 eV for the bond dissociation energy of F_2.

Failure to detect BrF_5^+ in the BrF_5 spectrum may be explained by reaction (8) going with a much higher probability than simple ionization of BrF_5. If reaction (8) is the initial step in the ionization process to the exclusion of formation of BrF_5^+ then for BrF_3 a probable overall reaction mechanism is

$$BrF_5 \rightarrow BrF_3^+ + F + F^- \quad (9)$$

the alternative reaction

$$BrF_5 \rightarrow BrF_3^+ + 2F \quad (10)$$

may be computed using the ionization potential of BrF_3, from the BrF_3 data, and Br—F bond energies and one finds that this requires 17·1 eV with only 15·5 available

in the appearance potential. Reactions involving loss of F_2 or F_2^- require less energy than (9), but cannot take place if the initial step in dissociation is reaction (8).

The differences in appearance potentials between BrF_2^+ and BrF_3^+ in both BrF_3 and BrF_5 spectra are nearly the same, 0·6 eV. This would support a production mechanism of BrF_2^+ from BrF_5 that would have as its final step

$$BrF_3^+ \rightarrow BrF_2^+ + F \qquad (11)$$

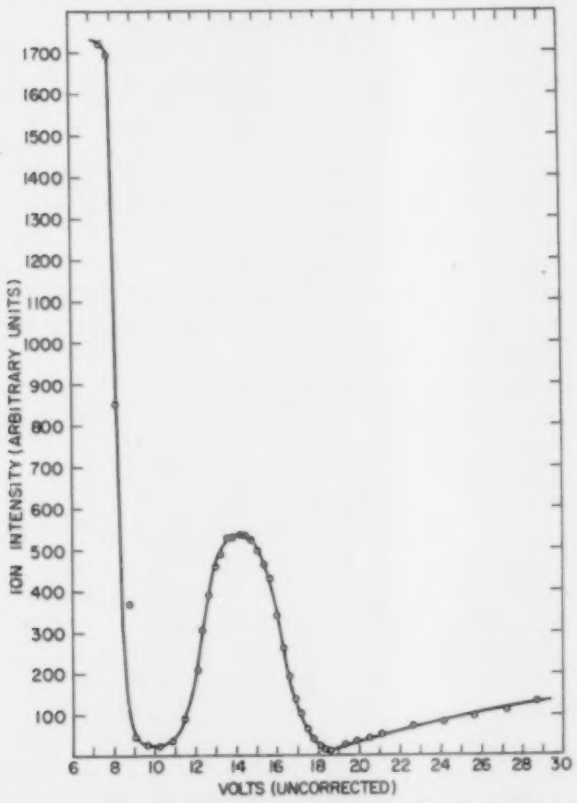

FIG. 13.—Ionization efficiency curve of F^- from BrF_3.

This type of sequential unimolecular decomposition mechanism would be favoured over reactions involving loss of F_2 or F_2^- if spectra were considered from the standpoint of the statistical theory of mass spectra,[5] and is consistent with ionization efficiency curves showing one ionization process for the formation of BrF_4^+, BrF_3^+ and BrF_2^+ in the BrF_5 spectrum.

Interpretation of IF_5 dissociation mechanisms and estimation of ionization potentials of dissociation fragments from IF_5 is made difficult by lack of an independent IF_3 spectrum which could give IF_3 and IF_2 ionization potentials. Ionization efficiency curves previously discussed suggest formation of these ions by relatively low-probability and lower-energy processes as well as by one type of higher-energy mechanism.

[5] (a) H. M. ROSENSTOCK, A. WALLENSTEIN, A. WAHRHAFTIG and H. EYRING *Proc. nat. Acad. Sci., Wash.* **38**, 667 (1952).
(b) L. FRIEDMAN, F. A. LONG and M. WOLFSBERG *J. chem. Phys.* In press.

This may be a result of trace amounts of IF_3 impurity or infrequent dissociations via loss of F^- ions. If one arbitrarily excludes IF_3 as an impurity and assumes the reactions

$$IF_5 \rightarrow IF_4^+ + F^- \quad (12)$$

$$\rightarrow IF_3^+ + F^- + F \quad (13)$$

$$\rightarrow IF_2^+ + F^- + 2F \quad (14)$$

then upper limits for the ionization potentials of IF_4, IF_3 and IF_2 are estimated at 14·5 eV, 9·7 eV and 10·7 eV respectively. Alternative values may be derived from other assumed mechanisms which will be generally lower than those reported above.

Diatomic molecules

Good agreement has been demonstrated between electron impact appearance potentials and independently determined ionization potentials for the diatomic halogens.[6] The appearance potentials for Br_2^+ reported in the BrF_3 data agrees well with the earlier determination. Ionization potentials of the diatomic interhalogens may be used with atomic ionization potentials and bond dissociation energies to compute dissociation energies of molecule ions. Molecule ion dissociation energies for the homonuclear halogens are all 1–1·5 eV greater than corresponding neutral molecules. The diatomic interhalogens with the exception of BrCl all have ion dissociation energies equal, within experimental error, i.e. ~0·2 eV, to corresponding neutral molecule bond energies.

This difference in properties of molecules, isoelectronic in their valence shells, may be explained by noting that the polarization of the molecule XF makes X positive and that this would necessarily raise the ionization potential of X electrons in XF above that of X electrons in X_2.

An alternative way of describing the phenomenon is to note that in Cl_2, ionization involves loss of strongly antibonding electrons while in ClF the structure is such that non-bonding electrons are removed. The fact that the ClF bond energy is closer to Cl_2 rather than F_2 may be construed as meaning weaker antibonding of $p\pi$ electrons in ClF than Cl_2. This was found to be the case if one computes $2p\pi$–$3p\pi$ overlap integrals for ClF and compares them with the $3p\pi$–$3p\pi$ overlap integral in Cl_2. This was done using tables of overlap integrals of MULLIKEN *et al.*[7] The argument of MULLIKEN[8] for the relative bond strength of Cl_2 over F_2, namely that a small amount of $3d$ hybridization with second-row and higher elements strengthens second-row and higher bonds, also helps lower the antibonding in ClF. Thus molecular orbital considerations qualitatively indicate the direction of the effect. A reliable explanation, however, must wait on a detailed and exhaustive computation.

Acknowledgements—The authors wish to express appreciation to JOHN SPEIRS and GERALD STRICKLAND, of the Nuclear Engineering Department of Brookhaven National Laboratory, for their co-operation and advice throughout the course of this work.

[6] J. D. MORRISON and A. J. C. NICHOLSON *J. chem. Phys.* **20**, 1021 (1952).
[7] R. S. MULLIKEN, C. A. RIEKE, D. ORLOFF and H. ORLOFF *J. chem. Phys.* **17**, 1248 (1949).
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THE SZILARD–CHALMERS REACTION IN FERROCENE*

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Abstract—The products of the Szilard–Chalmers reaction in ferrocene have been separated by solvent extraction and chromatography. For samples irradiated in the centre of the Brookhaven reactor about 12 per cent of the ^{59}Fe activity is found in the form of the parent compound. The yield is increased to about 21 per cent by heating the irradiated samples. The yield of inorganic radioactive iron is decreased by thermally annealing the irradiated crystals; this effect appears to depend on the fast-neutron dose received by the sample during activation. The distribution of radioactive products is not altered by exposing the sample to large doses of γ-radiation after activation in the reactor.

An explanation of the results is offered, which suggests that the following types of fragments are formed in the crystals during pile-irradiation: free iron atoms or ions and iron-mono*cyclo*pentadienyl radicals as primary disruption products in the (n, γ) processes; free *cyclo*pentadienyl radicals, C_5H_5; and organic radicals formed by rupture of the C_5H_5 rings in ferrocene when fast neutrons are present.

THE Szilard–Chalmers reaction has been investigated in a large number of organo–metallic compounds and metal complexes.[1–5] Yields of activity in the form of the parent molecule (often referred to as "retention") are usually about 2–5 per cent for irradiations of the solid compound in the thermal column of a reactor, while aqueous extracting agents can generally remove 50–80 per cent of the activity. The fraction of the activity found in the parent species may be increased by heating the irradiated crystals or by exposing them to radiation.

We have studied the Szilard–Chalmers reaction in ferrocene (bis*cyclo*pentadienyl iron (II)) in order to determine the chemical fate of the radioactive iron and to ascertain whether there would appear any effects ascribable to the unusual structure and stability of the compound.

EXPERIMENTAL

The ferrocene was synthesized from sodium *cyclo*pentadienide and ferrous chloride in tetrahydrofuran solution. The product was purified by sublimation followed by recrystallization several times from alcohol–water mixtures.

About 500 mg of ferrocene were sealed off *in vacuo* in silica ampoules for irradiation in the Brookhaven reactor. The various samples were irradiated in the thermal column and in the water and air-cooled facilities of the pile.

After irradiation and any subsequent treatment or ageing which were to be employed in a particular case, the sample was separated into various fractions. The

* Research performed under the auspices of the U.S. Atomic Energy Commission.

(1) R. R. WILLIAMS, JR., G. H. JENKS, W. B. LESLIE, J. W. RICHTER and Q. V. LARSON *Radiochemical Studies: The Fission Products* Book I, p. 184. McGraw-Hill, New York (1951).
(2) W. HERR *Z. anorg. Chem* **258**, 94 (1949).
(3) H. SPANO and M. KAHN *J. Amer. chem. Soc.* **74**, 568 (1952).
(4) A. G. MADDOCK and N. SUTIN *Trans. Faraday Soc.* **51**, 184 (1955).
(5) R. M. S. HALL and N. SUTIN *J. inorg. nucl. Chem.* **2**, 184 (1956).

radioactivity of each fraction was determined by counting. In general, the counting was performed on solutions (in water, acetone, or hexane), with a glass-walled Geiger–Müller counter of the immersion type. Under these conditions essentially all of the recorded counts were due to the 1·10 and 1·30 MeV γ-rays of ^{59}Fe, and no corrections for self-absorption were necessary. The same activity ratios between the various fractions were found when the solutions were counted in a thick-walled glass container with a sodium iodide scintillation counter.

The fractionations were carried out as follows.

The irradiated samples were dissolved in 30 ml of hexane and extracted four times with 25 ml portions of 0·1N HCl. The addition of ferrous sulphate carrier did not increase the proportion of extractable activity. A further 5 per cent of the activity could generally be extracted into the aqueous phase when ferric chloride was added. However, it was evident from the blue colour of the aqueous phase that oxidation of the ferrocene to ferricinium chloride occurred under these conditions, which could account for the observed increase. In view of these facts, the extractions were done without added carrier.

When the aqueous extract was to be assayed for activity present as ferric ion or forms exchangeable with ferric ion, ferric perchlorate carrier was added, and the inorganic iron was separated by precipitating ferric hydroxide with ammonium hydroxide. The precipitate was centrifuged off, dissolved in dilute hydrochloric acid; then the iron was reprecipitated as the hydroxide and redissolved in 8M HCl. The ferric chloride was extracted into 30 ml of *iso*propyl ether and finally back-extracted into water and counted. In general, however, the aqueous phase was counted without these further purifications.

The hexane layer was chromatographed on alumina. The ferrocene was eluted with additional hexane, and oxidized to ferricinium with silver sulphate and dilute sulphuric acid. Excess silver was removed by precipitating the chloride. Sodium silicotungstate was added to precipitate ferricinium silicotungstate which was centrifuged off and converted to the perchlorate by shaking with concentrated perchloric acid. The silicotungstic acid was centrifuged off, the ferricinium ion reduced to ferrocene with stannous chloride, and the cycle repeated. The specific activity was not changed by the second cycle. It was found that a steam distillation step preceding the oxidation to ferricinium did not affect the final specific activity.

It was found that after the hexane extraction considerable activity was recoverable from the walls of the separatory funnel by washing with acetone. Subsequent washings with chromic acid or with sodium hydroxide solution contained no activity.

Preliminary experiments failed to detect any exchange between ferrocene and ferrous ions, while the exchange between 10^{-4}M solutions of ferrocene and ferricinium ions was found to be complete within a few seconds at room temperature.

RESULTS AND DISCUSSION

Chemical forms of the iron activity

As a result of the procedure described, activity measurements were obtained on three crude fractions of the sample; a water-soluble fraction, a hexane-soluble fraction, and a fraction insoluble in hexane or water but soluble in acetone. We take the sum of these as the total activity of the sample. This was shown to be the case in a separate experiment in which the total activity was separately measured on an

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ethanol solution of a portion of the irradiated ferrocene and compared with the sum of the aqueous, hexane, and acetone fractions. The agreement was within 1 per cent. The further purification led to a fraction which followed the chemistry of ferric ion and one which followed the chemistry of ferrocene. The compounds present in the acetone fraction and those other than ferrocene in the hexane fraction have not been identified.

In this discussion our main attention will be given to the yields of the aqueous and ferrocene fractions, defined as the percentage ratio of the activity in each to the total activity in the original sample.

An analysis of a sample irradiated for 5 days at an average flux of $3{\cdot}6 \times 10^{12}$ thermal neutrons/cm^2 sec is given in Table 1. This analysis was performed shortly after irradiation. The aqueous fraction accounted for about half of the total activity; the ferrocene yield was about 13 per cent. The average specific activity for the total sample was 2010 counts/min per mg Fe; the specific activity of the aqueous fraction (no added carrier) was 31,930 counts/min per mg Fe.

TABLE 1.—ANALYSIS OF IRRADIATED FERROCENE

	Percentage of total activity	Specific activity (counts/min per mg Fe)
Aqueous layer	53·8	31,930
Hexane layer	25·1	
Acetone fraction	21·1	
Ferric chloride	49·2	
Hexane eluate	15·0	301
Ferricinium perchlorate (1)	12·8	257
Ferricinium perchlorate (2)	12·8	257

When a 10^{-2}M solution of ferrocene in *n*-hexane was irradiated for 4 days at a thermal neutron flux of $3{\cdot}6 \times 10^{12}$/cm^2 sec, the yield of radioactive ferrocene was not significantly different from zero. Aqueous extraction removed 68 per cent of the activity. Under these conditions the ferrocene molecule is disrupted in practically all of the neutron captures, and none of the active iron is subsequently reincorporated into ferrocene molecules. However, some 32 per cent is organically bound, in a form resistant to aqueous extraction. No attempt has been made to identify the state, or states, of combination of the iron in this fraction.

Effect of the conditions of irradiation

Table 2 shows the effect on the inorganic yield of various irradiation conditions. Two samples (numbers 1 and 2) were bombarded in the pile interior, one (number 3) in the graphite near the shield, and another (number 4) in the thermal column. Samples 3 and 4 showed a significantly higher inorganic yield than 1 and 2. The increase is not correlated with the slow-neutron flux or dose, rather it occurs when the fast-neutron and γ-ray doses are greatly reduced from the levels prevailing in the interior of the reactor.

A portion of sample 3 was submitted (sample 3a) to a heavy post-irradiation γ-ray dose of the same order of magnitude as the in-pile dose received by samples 1 and 2. The inorganic yield was altered by less than 1 per cent. We conclude that the lowered inorganic yield of the first two samples is due to the fast neutrons or, alternatively, that the inorganic yield is more sensitive to γ-rays during the activation than it is to post-irradiation γ-rays. The first possibility seems more likely.

Effects of thermal annealing

The yields of radioactive ferrocene (initially about 12 per cent) from samples 1, 2, and 3 were found to increase with time when the samples stood at room temperature, reaching about 19 per cent after 6 weeks. During the same period the inorganic yield decreased by less than 1 per cent. The ferrocene yield of sample 4, which had been activated in the thermal column, rose only to 14·4 per cent in 6 weeks. The ferrocene yield of a sample irradiated one day in the reactor at liquid-nitrogen temperature was found to be 8·9 per cent shortly after the irradiation, and rose to 14·3 per cent on standing for 6 days at room temperature.

TABLE 2.—VARIATION IN THE YIELD OF AQUEOUS EXTRACTABLE ACTIVITY WITH CONDITIONS OF IRRADIATION

Sample	Time in reactor (days)	Thermal neutron flux nv (cm^{-2} sec^{-1})	Approximate fast-neutron exposure* nvt (cm^{-2})	Approximate γ-ray dose* (r)	Extractable activity (%)
1	5	$3{\cdot}6 \times 10^{12}$	160×10^{16}	270×10^{6}	53·8
2	7	$2{\cdot}6 \times 10^{12}$	160×10^{16}	230×10^{6}	52·4
3	10	1×10^{12}	4×10^{16}	60×10^{6}	61·0
3(a)†	10	1×10^{12}	4×10^{16}	60×10^{6}	60·5
4	40	5×10^{8}	5×10^{11}	1×10^{5}	63·2

* Estimated from data given in *Research Reactor Facility*. Brookhaven National Laboratory (August 1956).

† A portion of sample 3 exposed to 600×10^{6} r of ^{60}Co γ-radiation after activation.

Thus, radioactive ferrocene must be formed after irradiation by temperature-sensitive reactions. These reactions presumably are also proceeding during bombardment. Since the inorganic yield is essentially constant during the moderate annealing just described, we infer that the iron which is reacting to form ferrocene does not come from the pool of entities comprising the aqueous-extractable iron. The result with sample 4 indicates that the entities with which the iron is reacting to give ferrocene are less available in a sample activated in the thermal column. We suggest that these entities are not fragments generated in the local zone of damage by the recoiling ^{59}Fe, but that they are produced by γ-rays or fast neutrons, or both, in samples 1, 2, and 3.

In a more systematic study of post-irradiation thermal annealing, the ferrocene yield and the inorganic yield for samples 1, 2, and 3 were determined as functions of heating time at elevated temperatures. Sample 1 was annealed at 60°C. Sample 2, which had been activated under approximately the same conditions, was annealed at 110°C; and sample 3, which had received considerably smaller fast-neutron and γ-ray doses, was also annealed at 110°C. The results are shown in Figs. 1 and 2.

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In Fig. 1 the annealing behaviour at 110°C is shown for samples 2 and 3, exposed under very different irradiation conditions. The most striking feature of the results is the precipitous decline of the inorganic yield in the first hour of heating of the sample which had received a heavy exposure of fast neutrons and γ-rays. On the

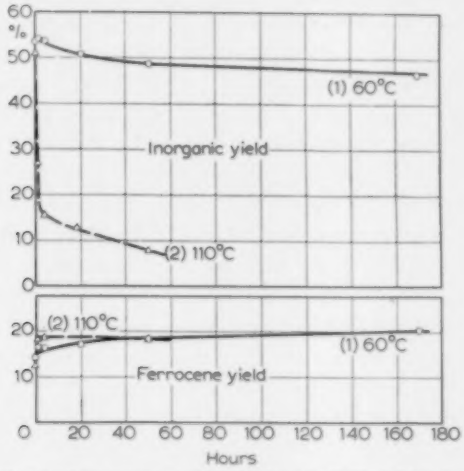

FIG. 1.—Effect of fast-neutron exposure on annealing at 110°C. (Triangles represent sample 2, which received large fast-neutron dosage; circles sample 3, low fast-neutron dosage.)

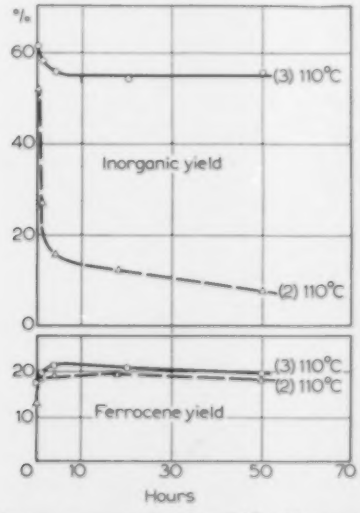

FIG. 2.—Annealing at different temperatures of samples with comparable fast-neutron dosage.

other hand, the inorganic yield of the sample with reduced γ- and fast-neutron exposure shows only a modest decline in the first few hours and is thereafter constant. We infer, as from the observations at room temperature, that the entities with which iron reacts in leaving the pool of aqueous-extractable iron are available to a much greater degree in the sample which received the high dose of fast neutrons and γ-rays.

These reactions clearly lead to products other than ferrocene, since the ferrocene yields do not change correspondingly during annealing.

In Fig. 2 is shown the annealing behaviour at two different temperatures of samples 1 and 2, which had comparable irradiation history. The great effect of annealing on the inorganic yield is developed only at the higher temperature, 110°C. At 60°C there is an apparent levelling-off after a moderate initial decline.

The yield of radioactive ferrocene is somewhat dependent on the conditions of irradiation, but less strikingly so than the inorganic yield. With the samples under discussion the ferrocene yield rose with annealing to a value in the neighbourhood of 20 per cent in each case. The rise is much more rapid at 110°C. There is apparently a slight decrease in the retention on continued heating at 110°. Since the specific activity of the ferrocene did not undergo a corresponding decrease, this fall is most likely due to slight decomposition of the ferrocene during the heating period. The annealing of the radioactive iron thus takes place while the sample itself is decomposing.

The question arises whether the fast-neutron effect is associated with the larger recoil energy imparted to the iron nucleus by fast-neutron capture, or whether it is a radiation chemical effect associated with radiation damage to the bulk sample. We favour the second possibility, on the basis of an experiment in which the proportion of ^{59}Fe produced by fast neutrons was determined. Two iron foils were irradiated in the same position in the pile as the first sample of ferrocene. One of the foils had been wrapped in cadmium so that the thermal neutrons were filtered out. The activities of the irradiated foils were compared. It was found that the wrapped foil had 5·6 per cent as much ^{59}Fe activity as the unwrapped foil. This amount is too small for an effect of recoil energy to account for the large difference observed in the annealing properties of the samples. This follows, since the fraction of radioactive iron atoms in ferrocene resulting from fast-neutron capture is so small, and since the energy input from these recoils is a negligible fraction of the total energy input (fast neutron and γ's) to the system. We conclude that the observed effect is attributable to radiation damage caused by the fast neutrons.

REMARKS ON MECHANISM

The recoil is expected to lead to bond rupture in every neutron capture; the result of the irradiation of a solution of ferrocene in hexane confirms this expectation. It does not necessarily follow that every (n, γ) process results in bond rupture in the solid phase. However, the lowest ferrocene yield found in this work was 8·9 per cent, and it seems justified to conclude that "original retention," i.e. the occurrence of radioactive iron attached to its original bond partners, is certainly less than this value. We may assume for the present discussion that the original molecule is always disrupted. One must then account for the three (or more) different chemical forms in which the radioactive iron is found, for the effect of fast neutrons, and for the effect of annealing. We suggest that the essential features of the results can be understood in terms of: the disruption of the ferrocene molecule into fragments by the (n,γ) process; the production of various molecular fragments in the track of the recoiling iron atom; the production of various organic radicals by the γ-rays and fast neutrons to which the sample is exposed; and reactions of the iron-containing fragment resulting from the (n, γ) process with such radicals.

In regard to the events which occur during the slowing-down process, the picture

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previously proposed[4] for other organometallic compounds may also be applicable to this system. In pure ferrocene the recoiling iron atom disposes of its excess kinetic energy in collisions with the surrounding molecules. At the beginning of its track, while it is still highly energetic, collisions with individual carbon atoms can lead to rupture of the *cyclo*pentadienyl rings. This effect is not expected to be large, for results[5] with triphenylarsine and triphenylstibine indicate that in these systems fragments resulting from the rupture of the aromatic rings constitute less than 20 per cent of the radioactive products. It is probable that some *cyclo*pentadienyl radicals will be formed in the recoil track, since the recoiling iron atom can lose energy very efficiently in collisions with other iron atoms. Towards the end of its track, the recoiling iron atom can undergo inelastic collisions with the ferrocene molecule as a whole, and this might lead to rupture of iron-*cyclo*pentadienyl bonds by vibrational excitation. It is likely that the final chemical form of the radioactive atom in the absence of radiation decomposition will be determined mainly by the nature of the reactions it undergoes with these excited molecules and fragments formed toward the end of its track. Part of the radioactive ferrocene (less than 8·9 per cent) may be produced in this way. As is evident from the results, recombination reactions also occur in the thermal region, since the retention rises on standing at room temperature.

It is suggested that the iron-containing fragments existing at the end of the slowing-down process are predominantly free iron atoms, or ions, and mono*cyclo*pentadienyl iron radicals. We also suppose that radiation damage leads to, among other entities, C_5H_5 (*cyclo*pentadienyl) radicals. The rise of the ferrocene yield during annealing is attributed to the combination of these with FeC_5H_5 radicals. We prefer this to the alternative that a free iron atom reacts successively with two C_5H_5 radicals, since the latter is a higher-order process, and because it is difficult to see how the latter mechanism could lead to a ferrocene yield so nearly constant at 21 per cent as that observed under a variety of conditions in the cases of samples 1, 2 and 3. On the other hand, if we suppose that the FeC_5H_5 radical is formed with some definite probability (determined by the dynamics of the recoil and the crystal environment), this feature of the results is accounted for. On this view one would expect that the ferrocene yield would be limited by the number of mono*cyclo*pentadienyl radicals formed in recoil, would approach a constant value when the radiation damage was sufficient to form enough C_5H_5 radicals to react ultimately with all of these, but would be less than this value when the radiation damage was less. This picture accounts both for the fact that the maximum ferrocene yield is essentially constant for irradiations in the pile, and for the fact that it was substantially less for the sample irradiated in the thermal column (gross radiation dose about 0·3 per cent of that received in the pile). In the latter case, the number of C_5H_5 radicals formed by gross radiation damage was evidently insufficient to insure the reaction of all of the FeC_5H_5 fragments to re-form ferrocene.

The effect of fast neutrons may now be considered. Since the samples irradiated in the centre of the pile absorbed roughly the same amount of energy[6] from the γ-radiation as from the fast neutrons, our observations suggest that for a given amount of energy absorption in ferrocene the fast neutrons produce different chemical effects than do γ-rays. The mechanism of the energy loss by knock-on protons and fast

[6] D. M. Richardson, A. O. Allen and J. W. Boyle *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955 Vol. 14, p. 209. United Nations (1956).

electrons is qualitatively similar, differing largely in the distribution of the clusters of ions and radicals along their tracks. It seems unlikely that such differences in the density of ionization could affect the final distribution of the radioactive iron. It seems more likely that the fragments produced in the collisions of the fast neutrons with atoms other than hydrogen are responsible for the difference between the effect of fast neutrons and γ-rays. We suggest that the fast neutrons by collisions with carbon atoms rupture the C_5H_5 ring and produce organic radicals other than *cyclo*-pentadienyl. The reactions of these entities with iron atoms or iron-containing fragments resulting from the (n, γ) process will lead to organically bound iron other than ferrocene. We suggest that such reactions are responsible for the pronounced drop in inorganic yield with annealing at 110°C for the sample which received a high dose of fast neutrons. The inorganic fraction consists, then, of free iron atoms and products arising from iron-containing radicals which have escaped stable organic combination and which are extractable from hexane by an acidic aqueous solution.

Support for the plausibility of the view that fast neutrons cause ring rupture is found in the work of SWORSKI and BURTON.[7] They report different distributions of products in the radiolysis of aromatic hydrocarbons, depending on whether the irradiations are carried out in the pile or with electrons. In the case of toluene these differences may be related to the larger extent of rupture of the phenyl ring occurring in the pile irradiations.

The necessarily speculative picture just presented accounts qualitatively for the main features of our results. We are under no illusions that the results are sufficient to prove the model, but hope that further studies will be suggested by them and by the interpretation given.

[7] T. J. SWORSKI and M. BURTON *J. Amer. chem. Soc.* **73**, 3790 (1951).

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INFRA-RED SPECTRA OF INORGANIC SOLIDS—III

OCTACYANO COMPLEXES OF TUNGSTEN(IV), (V), AND MOLYBDENUM(IV), (V), DIHYDRATE AND ANHYDROUS

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Abstract—Eight octacyano complexes of tungsten and molybdenum were scanned in the infra-red from 2 to 32 μ (5000 cm^{-1} to 300 cm^{-1}). For the scan, the KBr disk technique was employed. A special modification of the technique was devised in preparing the anhydrous samples for the infra-red examination. The spectra for the dihydrate complexes showed two sharply resolved O–H stretching vibration bands. A splitting of the C≡N stretching vibration band was observed for the dihydrate samples. Upon sample dehydration, the splitting was less prominent and a strong intensity band observed in the spectra of the dihydrate samples around 25 μ (400 cm^{-1}) was shifted to longer wavelengths.

IN continuation of the infra-red study of inorganic materials,[1,2] eight octacyano complexes of tungsten and molybdenum were examined in the solid state from 2 to 32 μ (5000 cm^{-1} to 300 cm^{-1}).

EXPERIMENTAL

Preparations

The octacyano complexes of molybdenum and tungsten were prepared in this laboratory. The procedure for the molybdate(IV) complex is given in *Inorganic Synthesis*.[3] The procedure for the tungstate(IV) complex is given by OLSSON[4] as are the procedures for the molybdate(V) complex and the tungstate(V) complex.[5] The anhydrous samples were prepared from the dihydrate complexes by drying in a vacuum oven overnight at 100°.

Analytical methods

Analyses of the complexes were performed for nitrogen, water, tungsten, and molybdenum. Nitrogen was determined by the standard micro Dumas technique. Water was determined in the dihydrate complexes by a weight-loss on heating procedure.[3] Tungsten and molybdenum were determined as WO_3 by the usual HCl–cinchonine procedure and as $PbMoO_4$, respectively. Samples were prepared for analysis by digestion with hot concentrated nitric acid.

Tungsten and molybdenum in the oxidation state of (IV) were checked by a permanganate titration method.[3]

[1] E. G. BRAME, JR., S. COHEN, J. L. MARGRAVE and V. W. MELOCHE *J. inorg. nucl. Chem.* **4**, 90 (1957)
[2] E. G. BRAME, JR., J. L. MARGRAVE and V. W. MELOCHE *J. inorg. nucl. Chem.* **5**, 48 (1957)
[3] N. H. FURMAN and C. O. MILLER *Inorganic Synthesis* Vol. III, p. 160.
[4] O. OLSSON *Ber. dtsch. chem. Ges.* **47**, 917 (1914).
[5] O. OLSSON *Z. anorg. Chem.* **88**, 49 (1914).

Potassium octacyanomolybdate(IV) dihydrate, $K_4Mo(CN)_8,2H_2O$, light yellow, crystalline: Nitrogen, calc. 22·6 per cent, obs. 22·8 per cent: Molybdenum, calc. 19·34 per cent, obs. 19·40 per cent, 19·48 per cent, 19·58 per cent: Water, calc. 7·25 per cent, obs. 7·25 per cent, 7·35 per cent.

Potassium octacyanotungstate(IV) dihydrate, $K_4W(CN)_8,2H_2O$, light yellow crystalline: Nitrogen, calc. 19·2 per cent, obs. 19·3 per cent: Tungsten, calc. 31·5 per cent, obs. 30·6 per cent, 30·9 per cent: Water, calc. 6·16 per cent, obs. 7·08 per cent, 6·99 per cent.

Potassium octacyanomolybdate(V) dihydrate, $K_3Mo(CN)_8,2H_2O$, light yellow crystalline: Molybdenum, calc. 22·75 per cent, obs. 22·75 per cent, 23·00 per cent: Water, calc. 7·87 per cent, obs. 8·46 per cent, 8·65 per cent.

Potassium octacyanotungstate(V) dihydrate, $K_3W(CN)_8,2H_2O$, Tungsten, calc. 33·72 per cent, obs. 33·57 per cent, 33·63 per cent: Water, calc. 6·60 per cent, obs. 6·24 per cent, 6·22 per cent.

Sample preparations

The infra-red spectra were determined using the KBr disk technique.[6,7] A Nujol mull preparation was employed for checking the spectral results from the KBr disk technique. It was noted that the anhydrous samples rapidly absorbed moisture during the process of grinding and mixing, to form the dihydrate compounds. In order to minimize this interference, a Wig–L–Bug amalgamator, manufactured by the Cresent Dental Manufacturing Company, Chicago, Illinois, was used to grind[8] and mix the samples with the powdered KBr. About 2 mg of the dihydrate and 200 mg of powdered KBr were mixed for 5 min, after which the samples were placed in a vacuum oven and dried overnight at 100°. The mixture was removed from the steel cylinder of the instrument and transferred to the die in which the disk is formed. A minimum of contact with the atmosphere was achieved. Sample mixtures were pressed into disks under a total pressure of 10 tons for a period of 5 min. The disks were scanned from 2 to 16 μ with a Baird Associates, Model B, infra-red spectrophotometer and from 16 to 32 μ with a Perkin–Elmer model 112, infra-red spectrophotometer.

RESULTS

Spectra of the potassium octacyanomolybdate(IV) dihydrate and potassium octacyanotungstate(IV) dihydrate as well as their anhydrous complexes are reproduced in Fig. 1. Positions of band centres for the compounds investigated are presented in Tables 1–4. For the dihydrate complexes, bands observed in the 3 μ region were attributed to O—H stretching vibrations. In the 4–5 μ region, the observed bands were attributed to C≡N stretching vibrations. In the 6 μ region, a strong intensity band was attributed to an O—H bending vibration. Bands observed in the longer wavelength regions were not assigned. For the anhydrous complexes, only C≡N stretching vibrations were intense in the shorter wavelength regions. It was noted, however, that one of the three strong intensity bands observed in the 25 μ region (400 cm^{-1}) for the dihydrate complexes had shifted to longer wavelengths for the anhydrous complexes.

[6] U. SCHIEDT and H. REINWEIN *Z. Naturforsch.* **76**, 270 (1952).
[7] M. M. STIMSON and J. O'DONNELL *J. Amer. chem. Soc.* **74**, 1805 (1952).
[8] J. J. KIRKLAND *Analyt. Chem.* **27**, 1537 (1955).

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DISCUSSION

The band attributed to O—H stretching vibrations appears near 2·8 μ. For the dihydrates scanned here, an anomalous splitting is observed. For the molybdenum(IV) complex dihydrate, peaks are found at 2·78 and 2·83 μ. The structure of this material was examined by HOARD and NORDSIECK.[9] They concluded that no hydrogen bonding should occur between the water of hydration and the nitrogen of any cyanide

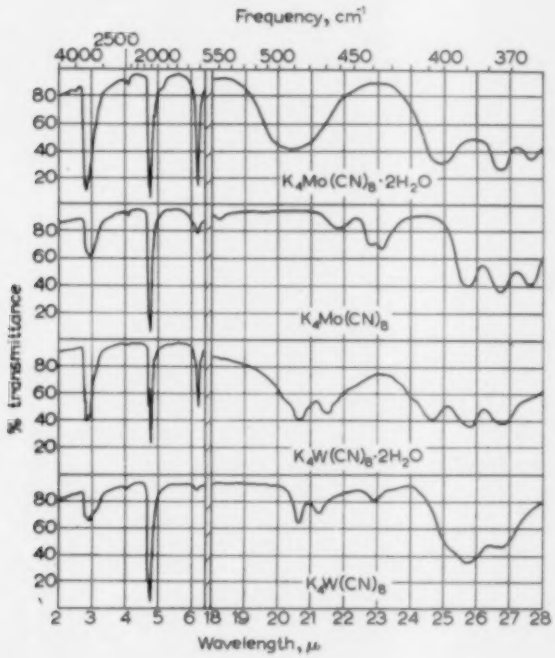

FIG. 1.

group, since the smallest O—N separation was 2·99 Å. However, WELLS[10] cites examples of hydrogen bonding in several amides in which the O—N distance ranges from 2·85 Å to 3·04 Å. Possible conflict between these two statements should be resolved by the infra-red spectra, since free hydroxyl groups show characteristic absorption at 2·70–2·80 μ, while hydrogen bonded O—H species absorb at wavelengths higher than 2·87 μ.[11] Hence it appears that the bands observed here are due to essentially free O—H vibrations, and that the observed splitting is due to crystal environment rather than a strong hydrogen bond. The relatively easy dehydration at 100° also argues against strong hydrogen bonding.

A splitting of the CN stretching vibration band into three peaks is observed in the 4–5 μ region for the dihydrate complexes. The crystal structure of potassium octacyanomolybdate(IV) dihydrate as determined by HOARD and NORDSIECK[9] gives three different C—N distances. Of the 8 cyanide groups, 6 have approximately

[9] J. L. HOARD and H. H. NORDSIECK *J. Amer. chem. Soc.* **61**, 2853 (1939).
[10] A. F. WELLS *Structural Inorganic Chemistry* p. 252, Table 16. Clarendon Press, Oxford (1945).
[11] L. J. BELLAMY *The Infra-red Spectra of Complex Molecules* p. 85. Methuen, London (1954).

Table 1

$K_4Mo(CN)_8,2H_2O$		$K_3Mo(CN)_8,2H_2O$	
Wavelength (μ)	Relative intensity	Wavelength (μ)	Relative intensity
2·78	strong	2·79	strong
2·83	strong	2·85	strong
2·90	shoulder	2·90	shoulder
4·06	very weak	4·06	very weak
4·72	strong	4·72	strong
4·77	strong	4·77	strong
4·88	medium	4·89	medium
5·00	shoulder	5·00	shoulder
6·19	strong	6·20	strong
20·2	strong	20·3	strong
24·9	strong	24·9	strong
26·7	strong	26·7	strong
27·6	strong	27·6	strong

Table 2

$K_4Mo(CN)_8$		$K_3Mo(CN)_8$	
Wavelength (μ)	Relative intensity	Wavelength (μ)	Relative intensity
2·92	medium	2·93	medium
4·70	shoulder	4·70	shoulder
4·75	strong	4·75	strong
5·85	weak	5·90	weak
6·20	weak	6·19	weak
18·2	weak	19·3	weak
19·5	weak	19·9	weak
21·8	medium	21·5	weak
22·8	medium	22·8	medium
23·1	medium	23·1	medium
25·7	strong	25·7	strong
26·7	strong	26·8	strong
27·6	strong	27·7	strong

Table 3

$K_4W(CN)_8,2H_2O$		$K_3W(CN)_8,2H_2O$	
Wavelength (μ)	Relative intensity	Wavelength (μ)	Relative intensity
2·80	shoulder	2·78	shoulder
2·85	strong	2·83	strong
2·92	strong	2·93	shoulder
4·05	very weak	4·05	very weak
4·72	strong	4·72	strong
4·79	strong	4·79	strong
4·90	shoulder	4·90	shoulder
6·20	strong	6·22	strong
20·6	srtong	20·6	strong
21·5	strong	21·4	strong
24·6	strong	24·7	strong
25·8	strong	25·7	strong
26·8	strong	26·7	strong

Table 4

$K_4W(CN)_8$		$K_3W(CN)_8$	
Wavelength (μ)	Relative intensity	Wavelength (μ)	Relative intensity
2·80	weak	2·80	medium
4·74	strong	4·70	shoulder
5·85	weak	4·75	strong
6·20	weak	6·20	medium
21·9	strong	20·8	medium
22·4	medium	21·4	weak
23·8	weak	22·5	weak
24·1	weak	23·1	weak
25·0	weak	24·1	weak
26·7	strong	25·8	strong
27·8	strong	26·9	strong

the same distance between the atoms, while the other 2 groups have different distances, 1 greater and 1 less than the 6 common distances. Thus the observed spectra correlate with the known structure of this complex ion.

On dehydration there is no decrease in intensity of the main cyanide band at 4·77 μ, but the 4·72 and 4·88 bands are greatly reduced in intensity and appear as shoulders on the main band. Since the removal of weakly held water could hardly be expected to cause the cyanide groups to become identical, the reduction in intensity of the 4·72 and 4·88 bands is probably due to a change in the relative transition

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probabilities for the 3 types of cyanide as a result of the removal of the water dipole.

A difference in position of the main C≡N vibration band appears for the tungstate(IV) dihydrate and the molybdate(IV) dihydrate samples. The band shifts to longer wavelengths between the molybdate(IV) and the tungstate(IV) complexes. The shift in band position is attributed to the difference in weight of the central metal ion. With a difference in weight, a difference in the frequency of vibration will result between the central metal ion and the bonded carbon atoms. A lower frequency of vibration will occur for the metal–carbon bond with an increase in weight of the metal ion. This lower frequency of vibration between the central metal ion and the carbon might produce a lowering of the frequency of vibration for the carbon–nitrogen bond, because the same carbon atom is involved in both vibrations. The weight is just about doubled between the molybdenum and tungsten atoms, so that it would seem that the effect of weight would be more predominant in shifting the frequency of vibration of the CN bond than any other factors might be. Therefore, the C≡N vibration band should be shifted to slightly lower frequencies for the tungstate(IV) complex than for the molybdate(IV) complex. This is what is experimentally observed.

HOARD and NORDSIECK[9] postulated that the tungstate(IV) dihydrate should be isomorphous with the molybdate(IV) dihydrate which they investigated. BAADSGAARD and TREADWELL[13] proved that the two were isomorphous. The very similar spectra of these two materials are in agreement with this structural isomorphism.

The remainder of the spectrum which was scanned to 32 μ showed a number of absorption bands. However, there was only one important relationship noted in the longer wavelength region. A shift of one of the strong absorption bands was observed between the dihydrate and the anhydrous samples. The others remained at the same positions. This shift of a strong band to longer wavelengths upon sample dehydration indicates that a structural change might be taking place. This assumption is based on the fact that skeletal vibrations are found to take place near the 25 μ region.[14]

The spectra of the oxidation-state 5 compounds showed peaks at identical wavelengths in the 2–7 μ region. In the longer wavelength region all of the same bands occurred, and the differences in peak wavelength and intensity were small.

[13] H. GAADSGAARD and W. D. TREADWELL *Helv. chim. Acta* **38**, 1669-79 (1955).
[14] D. M. SWEENY, I. NAKAGAWA, S. MIZUSHIMA and J. V. QUALIANO *J. Amer. chem. Soc.* **78**, 889 (1956).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 104 to 111. Pergamon Press Ltd., London

ANOMALIES IN THE INFRA-RED SPECTRA OF INORGANIC COMPOUNDS PREPARED BY THE POTASSIUM BROMIDE PELLET TECHNIQUE

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Abstract—Certain difficulties may be encountered when the potassium bromide pellet technique is applied to the infra-red examination of inorganic compounds. These difficulties are apparently due to an exchange of anions between the potassium bromide and the inorganic salt, and to pressure or orientation effects. The exchanges are illustrated by the use of infra-red spectra of a number of inorganic salts. For comparison purposes, the inorganic salts were also handled by the mull technique. The major factor responsible for exchange appears to be the moisture that is adsorbed on the surfaces of the sample and the potassium bromide.

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ANOMALIES in the infra-red spectra of inorganic salts handled by the potassium bromide pellet technique were noticed earlier by JOHNSON[1] and MEIKLEJOHN[2] of this laboratory. Due to the increasing interest in the potassium bromide technique, it was important to determine if these difficulties were widespread among inorganic salts and to evaluate the pellet technique in handling inorganic salts.

The majority of infra-red studies on inorganic salts up to this time were performed, using the Nujol mull or powder film methods of sampling.[3–6] In general, the potassium bromide pellet technique would offer the following advantages over these methods of handling solid materials:

1. The technique offers a basis for quantitative studies.
2. The spectra obtained are free from interfering Nujol bands in the 3·4, 6·8 and 7·2 μ regions.
3. Scattering at lower wavelengths, common in the powder film method, can be greatly reduced in most cases.
4. A sharper spectrum is usually obtained.
5. The pellet containing the sample can be preserved in a desiccator for future reference. Pellets kept in this way for long periods of time will become cloudy because of fissuring due to the relief of the strain set up in the crystal lattices. This fissuring causes extreme scattering in the lower wavelengths, but this scattering can be greatly reduced by reapplication of pressure to the pellet.

However, disadvantages in the use of this technique have been mentioned by PLISKIN and EISCHENS[7] and by KETELAAR *et al.*[8] In their examination of the spectrum

[1] D. R. JOHNSON Ph.D. Thesis, University of Wisconsin (1953).
[2] R. A. MEIKLEJOHN *Research Report* University of Wisconsin (1954).
[3] J. M. HUNT and D. S. TURNER *Analyt. Chem.* **25**, 1169 (1953).
[4] J. M. HUNT, M. P. WISHERD and L. C. BONHAM *Analyt. Chem.* **22**, 1478 (1950).
[5] J. LECOMTE *Cah. Phys.* **17**, 1 (1943), and references cited therein.
[6] F. A. MILLER and C. H. WILKINS *Analyt. Chem.* **24**, 1253 (1952).
[7] W. A. PLISKIN and R. P. EISCHENS *J. phys. Chem.* **59**, 1156 (1955).
[8] J. A. KETELAAR, A. C. HAAS and J. VAN DER ELSKEN *J. chem. Phys.* **24**, 624 (1956).

of ammonia chemisorbed to a catalyst, PLISKIN and EISCHENS found an absorption band at 7·1–7·2 μ. Previous investigators, using the powder film method, described this band at 6·9 μ. Further work indicated that the chemisorbed ammonia was combining with the potassium bromide to form ammonium bromide, accounting for this variation in the position of the absorption band. KETELAAR *et al.* attributed anomalies in spectra between pellet and mull technique to the formation of mixed crystals in their bifluoride–alkali halide system.

In our investigations on handling inorganic salts by the pellet technique, further disadvantages were encountered. In comparing spectra obtained by the use of the pellet technique with those obtained by the use of the mull, differences were noticed in some instances. These differences were attributed to an exchange of anions between the potassium bromide and the inorganic salts, and to pressure or orientation effects on the inorganic sample in the compressed pellet.

EXPERIMENTAL

Materials

Potassium bromide. Optical-grade potassium bromide is most suitable for use in making pellets. Ordinary reagent grades of potassium bromide were found unsuitable for pellet use because of slight organic and inorganic impurities which give rise to absorption bands near the 3·4, 7·0 and 9·0 μ regions. However, heating of this potassium bromide at 500–600°C overnight in a muffle furnace eliminates the majority of such impurities. Earlier experiments had demonstrated that heating at this temperature did not cause decomposition of the potassium bromide which was noticeable in the infra-red spectrum from 2 to 16 μ.

The potassium bromide particle size must be reduced to approximately 250-mesh in order to obtain transparent pellets. This reduction can be accomplished by grinding, freeze drying, or ethanol precipitation. Ethanol precipitation is advantageous in that it not only provides a rapid means of particle-size reduction, but it also reduces the soluble inorganic and organic impurities found in the unheated reagent-grade potassium bromide. After particle-size reduction by one of these methods, the potassium bromide was stored in a 120°C oven.

Inorganic salts. All inorganic samples were analytical reagent grade obtained from Merck, Mallinckrodt, or Baker. These inorganic salts were also heated in a 120° oven before use, except in cases where heat caused chemical or physical transformations resulting in altered constitutions or structures.

Procedure

All samples were run both as Nujol mulls and as potassium bromide pellets. Samples run as mulls were ground to a fine particle size in an agate mortar. One to two milligrammes of this finely powdered salt were then mixed with Nujol and placed between two rock-salt plates. Dispersion, and further particle-size reduction was accomplished by grinding the salt–Nujol mixture between two roughened salt plates. When the film was spread evenly between the plates, it was ready for examination. In many cases, these inorganic salts became imbedded in the rock-salt surfaces, necessitating regrinding of these surfaces before each new sample determination. Grinding for a short time with emery paper No. 2/0, was found satisfactory for complete removal of these imbedded contaminants.

Samples handled as pellets were prepared in the following manner: approximately 0·8–1·5 mg of the inorganic salt were weighed to the closest 0·05 mg and added to 300 ± 30 mg of potassium bromide delivered from a powder pipette. Mixing was accomplished by grinding in an agate mortar with a water-free solvent, such as $CHCl_3$, to insure a more homogeneous mixture and sharper spectrum.[9]

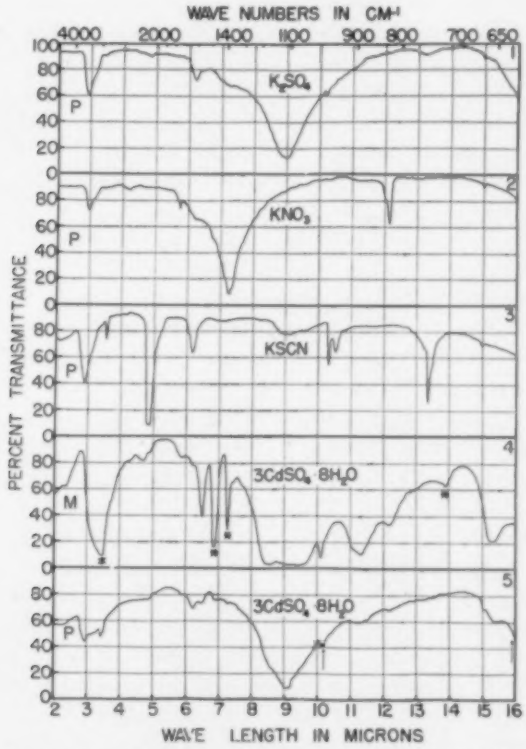

FIG. 1.—No. 1, potassium sulphate K_2SO_4, No. 2, potassium nitrate KNO_3, No. 3, potassium thiocyanate KCNS, No. 4, cadmium sulphate $3CdSO_4.8H_2O$ mull, No. 5, cadmium sulphate $3CdSO_4.8H_2O$ pellet.

All samples were examined as mulls and as potassium bromide pellets from 2 to 16 μ with a Baird Model B double-beam infra-red recording spectrophotometer.

RESULTS

Anomalous effects were observed for the infra-red spectra of inorganic salts handled by the potassium bromide pellet technique. These discrepancies were attributed to an exchange of anions taking place between the potassium bromide and the inorganic salt being examined, and to pressure effects on the sample in the compressed pellet.

A number of spectra illustrating exchange of anions are presented at the end of

[9] D. N. INGEBRIGTSON and A. L. SMITH *J. chem. Phys.* **26**, 1765 (1954).

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this paper. Spectra obtained by the mull technique are indicated by an *M*, and those by the pellet technique, by a *P*. Bands due to Nujol are marked by asterisks. The bands due to an exchange of anions are indicated by arrows. Spectra 1, 2 and 3 in Fig. 1 are of potassium salts, which are used as reference spectra to determine if exchange has taken place in certain systems.

Exchange between the bromide of potassium bromide and the anion of the inorganic sample was evident from the appearance of the potassium-anion spectrum superimposed on, or replacing entirely the spectrum of the inorganic sample. In some cases, exchange could be ascertained from the colour of the pellet; the colour indicating that the corresponding sample-bromide had been formed.

A total of approximately ninety salts was examined, representing the five groups discussed below.

Carbonates. Before preparation of the pellets, the carbonates were heated at 120°C to eliminate the majority of the surface moisture. Even though the moisture was largely removed, subsequent handling reintroduced a certain amount. The basic carbonates were not heated, for fear of any decomposition. The spectra obtained by the mull method and by the pellet method were identical for all the carbonates examined. There was no evidence of exchange taking place. The normal carbonates of silver, strontium, cadmium, cobalt(II), manganese(II), iron(II), magnesium, potassium, sodium, barium, calcium, lead and lithium, and the basic carbonates of copper, magnesium, nickel, chromium(III), beryllium and zinc were examined.

Phosphates. The phosphates were heated at 110°C before preparation of the pellets. The hydrated phosphates of lithium, sodium, magnesium, manganese(II), iron(III), cobalt(II), nickel, copper and zinc, and the anhydrous phosphates of potassium, calcium, strontium, silver, cadmium, barium, bismuth(III) and lead were examined. Comparison of the spectra obtained by the mull technique and the spectra obtained by the pellet technique indicated that none of the phosphates had exchanged anions with the potassium bromide.

Sulphates. The sulphates were heated at 120°C before preparation of the pellets. The hydrated sulphates of zinc, cobalt(II) and cadmium, and the anhydrous sulphates of mercury(II) and mercury(I) were not heated, because they either decompose or undergo transitions at low temperatures. A number of the sulphates examined exhibited signs of exchange. Nos. 4 and 5 in Fig. 1 show the spectra of hydrated cadmium sulphate as a mull and as a pellet. The band at 10·1 μ in both mull and pellet spectra is due to the hydrated cadmium sulphate, while the band at 10·2 μ in the pellet spectrum is caused by the potassium sulphate molecule. Further evidence of exchange can be seen by examining the 15–16 μ region. The mull spectrum shows an absorption band for the hydrated cadmium sulphate at 15·3 μ, while the pellet spectrum not only shows this same band, but also the start of the potassium sulphate band at 16 μ. This can be seen by comparison with No. 1, which is a spectrum of pure potassium sulphate. The hydrated sulphates of copper(II) and zinc, and the anhydrous sulphates of mercury(II), mercury(I), lead, copper(II) and silver also gave indications of a possible exchange taking place. The hydrated sulphates of manganese(II), cobalt(II), lithium, magnesium, nickel and calcium, and the anhydrous sulphates of sodium, strontium, and barium did not exhibit signs of exchange.

Nos. 6 and 7 in Fig. 2 show the spectra of anhydrous copper sulphate examined

as a mull and as a pellet. Upon application of pressure to the copper sulphate–potassium bromide mixture, a dark reddish brown pellet was formed. This colour was attributed to the formation of a copper bromide complex when a small amount of moisture is available. The potassium sulphate band at 10·2 μ can be seen in the pellet spectrum of this system. Bands are also present in this pellet spectrum that cannot be explained by the process of simple exchange. Re-examination of this same

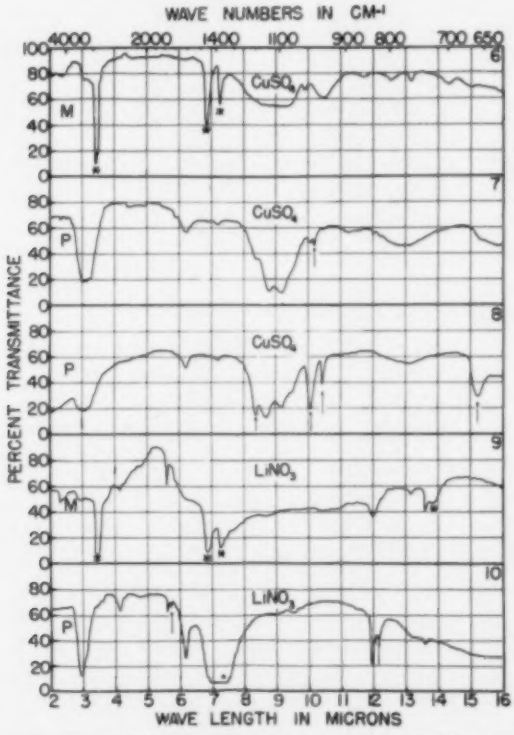

FIG. 2.—No. 6, copper sulphate $CuSO_4$ mull; No. 7, copper sulphate $CuSO_4$ pellet; No. 8, copper sulphate $CuSO_4$ pellet, after a lapse of time; No. 9, lithium nitrate $LiNO_3$ mull; No. 10, lithium nitrate $LiNO_3$ pellet.

pellet after a lapse of time (No. 8, Fig. 2) shows that there is an increase of some bands, and the appearance of new bands. Not enough work has been done to determine the source of the new absorption bands or the reason for the increase of the other absorption bands.

This copper sulphate–potassium bromide system demonstrated that the exchange is effected by the presence of surface moisture. Surface water was eliminated to a large extent by heating the salts at well over 100°C and mixing them at this temperature. The mixture was immediately pressed into a pellet which, when examined, showed only slight traces of exchange, distinguishable by scattered light brown regions due to the copper bromide complex formation. The spectrum of this pellet was identical to that of the mull; not enough exchange had taken place to be observed in the spectrum. If no precautions were taken to eliminate moisture, or if hydrated

copper sulphate was examined, dark brown pellets were obtained and exchange was observed from the spectrum.

Nitrates. The hydrated nitrates were not heated before examination, because the majority of them are subject to low-temperature transformations. The anhydrous nitrates of lithium, sodium, potassium, silver, strontium, barium and lead were heated at 120°C before preparation of the pellets. Approximately 50 per cent of those examined indicated that exchange had taken place. The 12·15 and 5·71 μ bands of potassium nitrate were quite noticeable. The following salts gave signs of exchange: cobalt(II) nitrate, lithium nitrate, bismuth(III) nitrate, zinc nitrate, iron(III) nitrate, mercury(II) nitrate, lead nitrate, silver nitrate, nickel(II) nitrate,

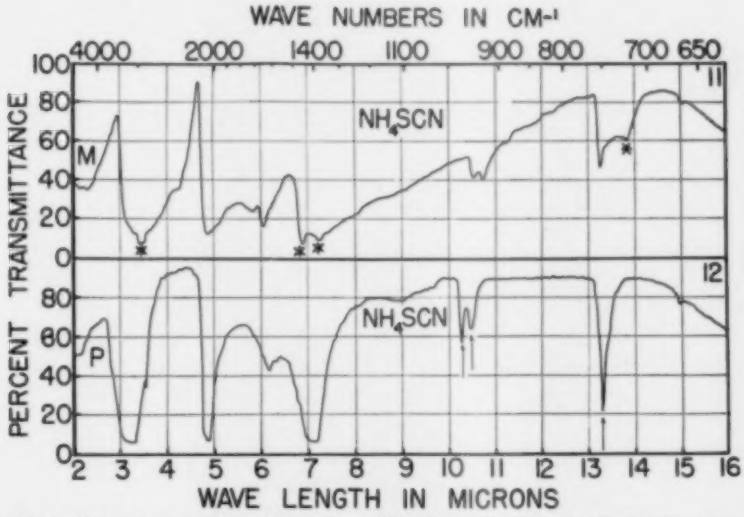

FIG. 3.—No. 11, ammonium thiocyanate NH_4CNS mull; No. 12, ammonium thiocyanate NH_4CNS pellet.

cadmium nitrate and magnesium nitrate. The spectra of lithium nitrate as a mull and as a pellet (Nos. 9 and 10, Fig. 2) are representative of the nitrate exchange. Comparison of the pellet spectrum with that of pure potassium nitrate (No. 2, Fig. 1) shows that exchange has taken place.

There was no indication of exchange for sodium nitrate, aluminium nitrate, calcium nitrate, chromium(III) nitrate, copper(II) nitrate, strontium nitrate, barium nitrate, thorium(IV) nitrate and mercury(I) nitrate.

Ammonium salts. Before preparation of the pellets, the ammonium salts, except the carbonate and molybdate, which decompose at low temperatures, were heated at 120°C. Several of the ammonium salts gave signs of exchange. Ammonium thiocyanate (Nos. 11 and 12, Fig. 3) is an example of an exchange with potassium bromide. Reference to spectrum No. 3 in Fig. 1 identifies the 10·3, 10·5 and 13·35 μ bands in the pellet spectrum of ammonium thiocyanate as bands due to potassium thiocyanate. Further investigations indicated that in this case, the mixing solvent, chloroform, was responsible for the exchange. When the ammonium thiocyanate and the potassium bromide were mixed together in the dry state, there was no evidence of exchange. When chloroform was employed as a mixing solvent, exchange was

noticeable. The exchange could have been brought about by the moisture which may have condensed on the salts as the chloroform evaporated. It is also possible that the chloroform itself acted as the agent of exchange, since thiocyanates are slightly soluble in organic solvents. Ammonium dichromate and ammonium sulphate also gave indications of an exchange. The spectrum of ammonium carbonate prepared as a pellet did not exhibit potassium carbonate bands, but rather bands due to potassium bicarbonate. The chromate, nitrate, molybdate, chloride, bromide and iodide did not exhibit any exchange noticeable from the positions of the absorption bands. However, exchange could not be observed for the halides, since the absorption bands arising from an exchange would fall too close to the original absorption bands to be distinguishable.

Potassium chloride pellets. All of the systems showing signs of exchange with potassium bromide were examined, using potassium chloride as the supporting medium. Similar exchange was observed in all cases.

Pressure effects

JOHNSON[1] noted changes in spectra of some of the ethylenediammine chelates of nickel(II) and copper(II) when handled by the pellet technique. He postulated that these changes were due to formation of another polymorphic form of the sample, or to strains set up in the crystal lattice of the sample, which is in this case less rigid than that of the potassium bromide. In our examinations of strictly inorganic salts, a shift in an absorption band was noticed for magnesium and lead nitrate, when the pellet technique was used. Ordinarily, these salts, examined as a mull, show an absorption band in the 12·3–12·6 μ region, but in the pellet form, this band appeared close to 12 μ. MILLER[6] mentioned this shifting as appearing in the mull spectrum of lead nitrate when it was prepared with different amounts of Nujol mineral oil. He concluded that it may be due to an orientation effect.

CONCLUSION

Although the potassium bromide pellet technique does possess advantages over other methods of handling solid materials, it is suggested that it be used with caution. In many cases, before accepting a pellet spectrum as being correct, its validity should be ascertained by other methods. This should especially be the case when working with inorganic compounds.

Factors responsible for this exchange and the amount of this exchange taking place are probably numerous, and related to type and size of ions, amount of pressure, time of application of pressure, size of particles, homogeneity of mixing, time expended in mixing, amount of surface moisture, and solubility of sample. It is believed that the major factor responsible for exchange is the moisture that is adsorbed on the surface of the samples and potassium bromide. We believe that this moisture serves as an agent of transfer of the ions in the pellets, resulting in the exchange. Work along these lines has indicated to us that in many cases, if precautions are taken to reduce the amount of surface moisture, the amount of exchange is greatly reduced and often eliminated completely. However, it is difficult to eliminate water entirely unless one resorts to extreme conditions. Furthermore, if one desires to examine a hydrated sample, or a sample which undergoes low-temperature transformations,

it is usually not possible to eliminate water without the sample undergoing some chemical or physical transformation.

It is difficult to predict which salts may be handled by the potassium bromide technique without difficulty. As a general rule, the more insoluble compounds suffer less from these exchange effects. However, there are exceptions to this rule. Lead sulphate, silver sulphate, and mercury(I) sulphate did exhibit signs of exchange.

It was found that it was difficult to reproduce exactly the spectrum of an exchange system. This would be expected, since the exchange seems dependent on a large number of variables which are difficult to control.

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INFRA-RED AND CRYSTALLOGRAPHIC INVESTIGATION OF THE TlCN–KCN–H_2O SYSTEM; THE LACK OF Tl(I)–CYANIDE COMPLEXES*

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Abstract—Infra-red, X-ray, and optical studies of solid phases obtained in the system TlCN–KCN–H_2O showed that no compound was formed between KCN and TlCN. Failure to find the compound $KTl(CN)_2$ is contrary to earlier work.[1] Solid solutions between TlCN + KCN were investigated in which Tl^+ substitutes for K^+ in the KCN structure up to a limit of ca. 37 mole per cent Tl^+. A new value for the cell dimension of TlCN was found, $a_0 = 3{\cdot}994 \pm 0{\cdot}001$ Å. Aqueous thallium(I) cyanide solutions containing a large excess of potassium cyanide (KCN/TlCN ratios as high as 100/1) gave no infra-red absorption peak ascribed to the $Tl(CN)_2^-$ anion. From the lack of effect of Tl^+ ion on the $Ag(CN)_3^- + CN^- \rightleftharpoons Ag(CN)_4^{---}$ equilibrium, it is shown that the value of the TlCN association constant, $TlCN/(Tl^+)\,(CN^-)$, is less than unity. Thus the thallium(I) ion has a smaller tendency to co-ordinate with cyanide ion than it does with chloride ion.

THE complexing properties of monovalent thallium are of interest, since it behaves in many cases as an alkali metal, such as potassium, and yet has some solubility properties similar to lead and silver. For example, although thallium(I) iodide is extremely insoluble, thallium(I) cyanide is quite soluble. As a heavy metal close to gold, mercury, and lead in the periodic table, even monovalent thallium might be expected to have some complexing properties.

The formation of Tl(I) chloride complexes has been well established by several workers. SCOTT and HU[2] report the following values: $Tl^+ + Cl^- = TlCl$, $K = 3{\cdot}8$; and $TlCl + Cl^- = TlCl_2^-$, $K = 0{\cdot}59$. From solubility measurements there is evidence for neutral molecules such as TlCl, TlOH, and TlCNS, with association constants of 4·8, 6·7 and 6·3, respectively.[3] At higher ionic strengths values are: TlCNS, $K = 2{\cdot}6$ ($\mu = 2$);[4] TlCl, $K = 1{\cdot}35$ and TlBr, $K = 0{\cdot}025$ ($\mu = 1{\cdot}2$).[5]

BASSETT and CORBET[1] reported the solid compound $KTl(CN)_2$ in their phase study of the system TlCN–KCN–H_2O at 25°C. This finding has been accepted as evidence for the formation of a thallium(I) cyanide complex ion in the solid. However, in an investigation of the TlCl–KCl system by X-ray methods, RUNCIMAN and STEWART[6] found that these chlorides form a limited series of *solid solutions*, with up to 15 mole per cent TlCl entering the KCl, substitutionally.

The absence of an aqueous thallous cyanide complex was commented on by

* This work was sponsored by the U.S. Atomic Energy Commission.
† Deceased.

(1) H. BASSETT and A. S. CORBET *J. chem. Soc.* **125**, 1660 (1924).
(2) A. B. SCOTT and KUO-HAO HU *J. chem. Phys.* **23**, 1830 (1955); *J. Amer. chem. Soc.* **77**, 1380 (1955).
(3) R. P. BELL and J. H. B. GEORGE *Trans. Faraday Soc.* **49**, 619 (1953); R. P. BELL and M. H. PANCKHURST *Rec. Trav. chim. Pays-Bas* **75**, 725 (1956).
(4) G. W. LEONARD, M. E. SMITH and D. N. HUME *J. phys. chem.* **60**, 1493 (1956).
(5) D. PESCHANSKI and S. VALLADÁS-DUBOUS *Bull. Soc. chim. Fr.* 1170 (1956).
(6) W. A. RUNCIMAN and E. G. STEWARD *Proc. phys. Soc.* A **66**, 484 (1953).

KOLTHOFF and MILLER.[7] In their study of the polarography of thallium(I) in aqueous KCN solution, they observed no chemical interaction between Tl(I) and cyanide ion.

Since the characteristic infra-red spectra of such cyanide anions as $Au(CN)_2^-$ and $Ag(CN)_2^-$, both in crystals[8,9] and in aqueous solution[10,11,12] have been observed, it was of interest to determine the infra-red frequency of the $Tl(CN)_2^-$ anion in the reported compound $KTl(CN)_2$ and, if possible, in aqueous solution.

EXPERIMENTAL AND RESULTS

Materials

Pure thallous cyanide was prepared by passing aqueous potassium cyanide solution through a large excess of cation exchanger (Dowex-50) in the thallium(I) form, followed by evaporation and recrystallization in the absence of air to avoid reaction with atmospheric CO_2 (the Tl^+-form resin was conveniently prepared by titrating a slurry of H^+-form resin with a TlOH solution until a slight permanent alkalinity was observed. The slurry was then poured into a column and washed with distilled water until the effluent was neutral). The Tl/K ratio of the product was shown to be $\gg$100/1 by spectroscopic analysis. Direct analysis for thallium and cyanide gave Tl = 88·7 (theory = 88·7) and CN = 10·7 (theory = 11·3). However, the thallium analysis is not very sensitive to the presence of Tl_2CO_3 in the crude product. X-ray and optical measurements were made on this analysed material, and again after recrystallization. The measurements showed that TlCN was the primary constituent of the first phase with a slight amount of Tl_2CO_3 present. Only the pure TlCN phase having properties reported in the following section was observed in the recrystallized material.

Reagent KCN (>99 per cent by assay) and CO_2-free distilled water were used.

Properties of thallous cyanide

The structure of thallous cyanide was reported previously by STRADA.[13] The simple cubic cell belongs to space group $O_h^1 - Pm3m$, and has the caesium chloride structure with one molecule of TlCN per unit cell. The cell dimension reported by STRADA is (after converting from kX to ängstrom units) 3·83 Å, considerably lower than the 3·994 $\pm$ 0·001 Å determined in the course of this study. However, STRADA's cell constant leads to a cation–anion distance and to a volume per formula unit which are practically identical with corresponding figures for thallous chloride. The dimensions calculated on the basis of the newly determined cell constant of thallous cyanide are substantially greater than those of thallous chloride; this is in agreement with the relation between corresponding compounds of some alkali metals (Table 1). This new value also agreed well with that predicted by WYCKOFF.[14]

Thallous cyanide crystals were obtained as large dendritic aggregates. The refractive index was found to be 2·02 $\pm$ 0·02 for sodium light by immersion in piperine–iodide melts. Experimental density determination using 4·4 g of TlCN in *sym*-tetrabromoethane yielded 5·96 g/cm^3 compared to the calculated value of 6·00 g/cm^3.

[7] I. M. KOLTHOFF and C. S. MILLER *J. Amer. chem. Soc.* **62**, 2171 (1940).
[8] L. H. JONES *J. chem. Phys.* **22**, 1135 (1954).
[9] L. H. JONES *J. chem. Phys.* **25**, 379 (1956).
[10] L. H. JONES and R. A. PENNEMAN *J. chem. Phys.* **22**, 965 (1954).
[11] R. A. PENNEMAN and L. H. JONES *J. chem. Phys.* **24**, 293 (1956).
[12] R. A. PENNEMAN, E. STARITZKY and L. H. JONES *J. Amer. chem. Soc.* **78**,62 (1956).
[13] M. STRADA *R. C. Accad. Lincei* **19**, 809 (1934).
[14] R. W. G. WYCOFF *Crystal Structures* Vol. I, Chap. III, Table, p. 23. Interscience Publishers, New York (1948).

TABLE 1.—COMPARISON OF X-RAY CONSTANTS OF SOME CYANIDES AND CHLORIDES

Compound	Cell constant a_0 (Å)	Distance R − X (Å)	Volume per formula unit (Å^3)
NaCN	5·893[15]	2·947	51·2
NaCl	5·6402[16]	2·820	44·9
KCN	6·527[15]	3·264	69·5
KCl	6·2931[15]	3·147	62·3
TlCN	3·994 (this paper)	3·459	63·7
TlCl	3·8421[17]	3·327	56·7

Attempted preparation of $KTl(CN)_2$

Using TlCN, KCN, and H_2O, an attempt was made to prepare $KTl(CN)_2$ according to the phase diagram of BASSETT and CORBET.[1]

Nine samples containing TlCN, KCN, and H_2O (insufficient water was weighed in to dissolve *all* the solids) (see Table 2) were prepared by accurately weighing each constituent into 3 ml tubes and equilibrated by rotating the sealed tubes end-over-end at room temperature (~25°C) for periods of 4 days. After this period the solid phases present were examined as will be described. Longer equilibration did not change the optical or X-ray properties of the solid phases. Some samples were "wet ball-milled" during equilibration by adding small agate balls to the tubes. This produced finer crystals and hastened attainment of equilibrium by grinding the solid phases while in contact with the mother liquor.

TABLE 2.—COMPOSITION OF SOLID PHASES IN THE SYSTEM TlCN—KCN—H_2O AT 25°

Composition of starting mixture, wt.%		Solid phases at equilibrium	Remarks
1. TlCN 1·14	KCN 43·9	Solid solution	Refractive index of solid solution phase only slightly higher than that of KCN. For properties of S. S. see Table 3.
2. 5·37	55·1	Solid solution	For properties of S. S. see Table 3.
3. 15·0	45·4	Solid solution	For properties of S. S. see Table 3.
4. 15·0	40·0	Solid solution	For properties of S. S. see Table 3.
5. 26·8	38·2	Solid solution	For properties of S. S. see Table 3.
6. 15·6	34·8	Limiting S. S and TlCN	Cell dimensions of TlCN in this two solid phase mixture same as pure TlCN. For properties of the limiting S. S. see Table 3.
7. 36·1	29·7	Limiting S. S. and TlCN	Cell dimensions of TlCN in this two solid phase mixture same as pure TlCN. For properties of the limiting S. S. see Table 3.
8. 24.6	28·1	TlCN	X-ray and optical properties of TlCN phase same as for pure TlCN.
9. 11·4	28·6	TlCN	X-ray and optical properties of TlCN phase same as for pure TlCN.

[15] H. E. SWANSON and E. TATGE *Standard X-ray Diffraction Powder Patterns* Vol. I. NBS Circular 539 (1953).
[16] H. E. SWANSON and R. K. FUYAT *Standard X-ray Diffraction Powder Patterns* Vol. II. NBS Circular 539 (1953).
[17] H. E. SWANSON, R. K. FUYAT and G. M. UGRINIC *Standard X-ray Diffraction Powder Patterns* Vol. IV. NBS Circular 539 (1955).

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Optical and X-ray results

To our surprise, it was found that samples 1–5 in Table 2 did *not* give two solid phases, KCN and $KTl(CN)_2$, as anticipated from the phase diagram in BASSETT and CORBET,[1] but gave in each case only one solid phase of variable composition and properties. Furthermore, samples 6 and 7 in Table 2 which should have produced $KTl(CN)_2$ as a single solid phase, gave *two* solid phases each having constant optical and X-ray properties. One of these solid phases was TlCN and the other a single phase containing TlCN at a mole fraction *significantly less* than corresponding to a 1/1 compound between KCN and TlCN. Samples 8 and 9 in Table 2 gave TlCN as indicated correctly.[1] It was evident that the workers[1] had erred in mistaking the KCN–TlCN solid solution as a single compound $KTl(CN)_2$, a mistake easy to make since they did not use the polarizing microscope or X-ray techniques. This is of considerable chemical interest since the "compound" $KTl(CN)_2$ is no longer valid.

Samples which were not ground during equilibration gave large (several tenths of a millimetre) cubic crystals which were not entirely homogeneous, exhibiting zonal textures with refractive indices variable within limits indicated in Table 3. The

TABLE 3

Sample		Cell constant a_0 (Å)	Refractive indices		Lorentz–Lorenz refraction (cm^3)	Estimated mole per cent TlCN*	
Number from Table 2	Description		n_D (range)	n_D (mean)			
—	Pure KCN	6·527[15]		1·413[15]	10·44	0	—
2	Solid solution	6·53 ± 0·01	1·413 – 1·45	$1·42_5$	10·7	3	—
3	Solid solution	$6·53_5$ ± 0·010	1·475 – 1·535	1·49	$12·1_5$	19	—
4	Solid solution	6·538 ± 0·003	1·495 – 1·525	$1·51_5$	12·7	25	—
5	Solid solution	6·543 ± 0·003	1·545 – 1·56	$1·55_5$	13·5	34	(31)†
6	Limiting S. S.	$6·54_5$ ± 0·010	1·56 – 1·58	$1·57_5$	$13·9_5$	39	—
7	Limiting S. S.	$6·54_5$ ± 0·010	1·56 – 1·59	$1·57_5$	$13·9_5$	39	—
—	Pure TlCN	3·994 ± 0·001		2·02	19·4	100	—

* Values were estimated by interpolation between molecular refractions of KCN and TlCN.
† Chemical analysis, see text.

inhomogeneity was responsible for diffuse lines of the powder X-ray diffraction patterns which made measurement of cell dimensions imprecise (±0·03 Å). This difficulty was minimized by having agate spheres present *during equilibration*. This "wet ball-milling" produced smaller, more homogeneous crystals which gave better X-ray patterns (samples having limits ±0·003 Å in Table 3). Optical and X-ray properties were determined on solid phases, both as a slurry in the equilibrium liquor and after being washed with alcohol after it was established that this procedure did not alter their properties. However, a thin surface film (probably KCN) remained coating the crystals of solid solution, making it necessary to crush them before determining the refractive index by the immersion method.

Near the limiting composition, but where only a single solid phase was still present, it was possible, by direct analysis, to check the estimation of TlCN in the solid solution made using optical and X-ray techniques. To accomplish this, a slurry sample was freed from mother liquor by a frit and the solid washed with alcohol. X-ray examination of the solid phase while still in contact with the mother liquor and after the above treatment showed no change. The solid was analysed for thallium and cyanide with the difference taken as potassium. This analysis gave 31 mole per cent TlCN and appears in the last column of Table 3, compared to 34 mole per cent estimated by the optical and X-ray method.

Pertinent crystallographic properties of several solid solutions and of the end members of the series are summarized in Table 3.

Infra-red measurements on solids

The samples of solid solution were separated from the mother liquor, dried, ground, and their spectra taken as a mineral oil mull, using the single-beam Perkin–Elmer Model 12-C recording infra-red spectrometer (converted to double-pass) and a LiF prism. The solid solutions gave a *cyanide* absorption peak only *slightly shifted* toward that of TlCN from that of pure KCN (see Table 4). No sharp, strong absorption band attributable to $Tl(CN)_2^-$ was obtained, contrary to the strong absorption observed in the case of the $Au(CN)_2^-$ and $Ag(CN)_2^-$ ions in solid compounds. This is further evidence that no complex thallium(I) cyanide anions are present in the solid phase.

TABLE 4

System	Position of absorption maxima (cm^{-1})
CN^- (aqueous)	2080 ± 1 * [10]
NaCN, solid	2090 ± 1
KCN, solid	2077 ± 1
TlCN, solid	2048 ± 1
Solid solution (~14 mole % TlCN)	2071 ± 2
Solid solution (~31 mole % TlCN)	2068 ± 2
$KAu(CN)_2$, solid	2141 ± 1 [10]
$KAg(CN)_2$, solid	2139 ± 1 [10]

* The absorption of cyanide ion is at the same position in aqueous TlCN as in aqueous LiCN, NaCN and KCN.

Infrc-red measurements on aqueous solutions

To check for the existence of $Tl(CN)_2^-$ in aqueous solution, a 0·15 M thallium (I) solution containing a mole ratio KCN/TlCN = 50 and another, 0·08 M thallium (I) at a mole ratio KCN/TlCN = 100, were examined in 30 μ path lengths in the infra-red by methods previously described.[10,11] Only the free cyanide ion absorption was present with no absorption attributable to $Tl(CN)_2^-$ being observed. The molar absorption coefficients of $Cu(CN)_2^-$, $Ag(CN)_2^-$, and $Au(CN)_2^-$ are all greater than 100 $moles^{-1}$ l. cm^{-1}.[10] Assuming that all the thallium was present as $Tl(CN)_2^-$ and that the limit of detection in 30 μ path length is 0·01 optical density units, the molar absorption coefficient of $Tl(CN)_2^-$ would have to be as low as 20 to escape detection. A solution of TlCN gives the unshifted CN^- absorption peak observed for aqueous NaCN, KCN, and LiCN (See Table 4).

Direct infra-red observation of the $Tl(CN)_2^-$ species would have been useful in setting a value for its formation constant. Failure to observe it can mean either that its extinction coefficient is small, much smaller than values observed for the $Cu(CN)_2^-$, $Ag(CN)_2^-$, and $Au(CN)_2^-$ series, or that $Tl(CN)_2^-$ has a small formation constant. Since a complex such as TlCN would be uncharged, its extinction coefficient would likely be very small, and direct observation by infra-red techniques even less likely.

Since direct observation of aqueous Tl(I)-cyanide complexes was not successful using infra-red techniques, an indirect method was tried. The effect of adding $TlClO_4$ to the NaCN–$NaAg(CN)_2$–H_2O system was studied. Since the $Ag(CN)_2^-$, $Ag(CN)_3^=$, and $Ag(CN)_4^{\equiv}$ equilibrium constants were previously determined by infra-red techniques,[10] an alteration in the system caused by a reaction between Tl^+ and CN^- could be calculated in terms of a constant for TlCN. Two solutions, each exactly 0·5 M $NaAg(CN)_2$, were made up. To each was added an identical amount of NaCN solution. Under these conditions the $Ag(CN)_2^-$ and $Ag(CN)_3^-$ ions gave distinct, well-separated absorption peaks, and there was 0·16 M free cyanide ion. One solution was 0·1 M in $TlClO_4$ (unfortunately, more thallium was not soluble in this system). We could easily have detected a diminution in free cyanide ion of 10 per cent. However, the ratio between the di- and tri-cyanide silver ions in the two solutions was identical, and was not altered by the presence of 0·1 M Tl^+. Consequently, we estimate a value for the quotient: $TlCN/(Tl^+)(CN^-) < 1$. Based on the usually stronger tendency of cyanide to complex compared with such anions as Cl^- and OH^-, it is perhaps surprising that Tl(I) and CN^- have so little interaction in aqueous solution.

DISCUSSION

Evidence has been presented showing that monovalent thallium does not possess appreciable complexing tendencies toward cyanide ion in either aqueous solution or solid phase, in contrast to the behaviour of its near neighbours in the periodic table—silver, gold, and mercury. On the contrary, Tl^+ can replace K^+ in solid KCN up to ~37 mole per cent TlCN and still retain the basic KCN structure. In this solid solution, there is no evidence of the formation of a $Tl(CN)_2^-$ anion. The phase diagram of Bassett and Corbet,[1] which indicates formation of $KTl(CN)_2$, is erroneous, since they misinterpreted the appearance of the solid solutions as indicating compound formation. It might be added that the use of a polarizing microscope, a relatively inexpensive tool, shows immediately by refractive index changes that compounds of fixed composition between KCN and TlCN are not present. In this study particularly, the refractive index change was so great that it was the solid solution characteristic most easily detected.

The fact that the cyanide absorption in the solid solutions is more closely related to that of cyanide in KCN rather than cyanide in TlCN arises because Tl^+ is substituting for K^+ in the KCN structure, and the *solid solutions retain the KCN structure* with a slightly increased cell constant. Note, for example, that the CN^- absorption is shifted even more (about 13 cm^{-1}) on going from NaCN to KCN, and both have the same crystal structure. Thus, we conclude that there is no more evidence of CN^- complexing with Tl^+ than there is for complexing with K^+ in these solid solutions.

The distances of CN^- ions from its six Na^+ or K^+ neighbours and its eight Tl^+ neighbours are 2·947 Å, 3·264 Å and 3·458 Å, respectively. The progression in CN^- ion frequency (NaCN > KCN > TlCN) parallels the increase in distance of the CN^- from the positive ions.

In their paper on the effect of cyanide on the rate of the Tl(I)—Tl(III) exchange, Penna-Franca and Dodson[18] postulate that Tl(I)-cyanide complexes such as TlCN, $Tl(CN)_2^-$, or $Tl(CN)_3^=$ may be formed at high CN/Tl(I) ratios. The present

[18] E. Penna-Franca and R. W. Dodson *J. Amer. chem. Soc.* **77**, 2651 (1955).

work and polarographic evidence show that formation constants for complexes between Tl(I) and cyanide ion must be quite small. It would be worth while if exact values could be obtained. Infra-red studies do not appear suitable for this purpose.

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Note added in proof: In a very recent paper, NILSSON[19] reports the formation constant of TlCN as *zero*, based on potentiometric measurements on the thallium(I)–cyanide system.

[19] R. O. NILSSON *Arkiv. Kemi* **10**, 363 (1957).

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HYDRIDE-TRANSFER REACTIONS OF BORINE—I

SYNTHESIS OF BORON-CARBON BONDS FROM THE FLUOROETHYLENES

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Abstract—The effect of diborane on four fluoroethylenes: tetrafluoroethylene, trifluoroethylene, 1:1-difluoroethylene and vinyl fluoride, has been studied at ordinary temperatures, and at higher temperatures. The reactions follow an essentially similar course, and in all cases complex mixtures are obtained. Fluorine in the ethylenes is first replaced by hydrogen, and boron in the products appears mainly as boron trifluoride, ethylboron difluoride, diethylboron fluoride and triethylboron. In the diborane-tetrafluoroethylene reaction polymerization of the olefin takes place with incorporation of some boron in the polymer. Moreover, distribution of boron in the volatile products is in the order $BF_3 > EtBF_2 \gg EtBF_2 > Et_2BF$. This order changes as the fluorine content of the olefin decreases. Thus with vinyl fluoride it is, $EtBF_2 > Et_2BF \gg BF_3 \sim Et_3B$.

The ethylboron fluorides are the main product of the reaction between tetrafluoroethylene, diborane and triethylboron.

Under conditions similar to those in which fluoroethylenes underwent complete reaction, diborane failed to react with saturated fluorocarbons such as ethyl fluoride.

A possible mechanism for the reactions between diborane and the fluoroethylenes is discussed.

DIBORANE reacts with a variety of electron-donor molecules able to promote dissociation of the hydride into borine‡ fragments. However, compounds containing unsubstituted borine groups are not always found as ultimate products of boron hydride reactions.[1,2] This is because co-ordination of BH_3 with donor molecules can sometimes be followed by elimination of molecular hydrogen, or by a hydride-transfer reaction. In either event, a BH_2-derivative is produced. Such derivatives polymerize, and, moreover, often also disproportionate, giving other products.

In the majority of cases so far investigated the hydride-transfer mode of decomposition proceeds so rapidly that isolation of the borine adduct is impossible. Nevertheless, its transitory existence may be inferred from the nature of the final reaction products, and by the known behaviour of BH_3 in other situations.

It is expected that this paper will be the first in a series concerned with the effect of borine, or its derivatives, on donor molecules where co-ordination is followed by rearrangement and disproportionation.

Olefins represent one class of donor molecule where treatment with borine leads to hydride transfer. Thus, diborane and ethylene yield triethylboron. It has been

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‡ It has been recommended by a nomenclature committee of the American Chemical Society that the BH_3 group be termed the borane group. See *Chem. Engng. News* **34**, 560 (1956). However, the Referees objected to the use of this new nomenclature in this paper, because the matter is still being debated.

[1] A. B. BURG *Rec. chem. Progr.* **15**, 159 (1954).

[2] F. G. A. STONE *Quart. Rev.* **9**, 174 (1955).

suggested[3] that this reaction proceeds through association of borine with *one* of the carbon atoms of ethylene, viz. $\overset{+}{C}H_2{\cdot}CH_2{\cdot}\overset{-}{B}H_3$. However, in comparison with other Group III acceptor molecules borine has an unusual co-ordination chemistry.[4] In view of this it is perhaps more likely that addition of borine to ethylene or other olefins occurs through a kind of π-complex intermediate in which a molecular bond orbital covers both carbon atoms and the boron atom at the same time.[5] In the case of ethylene, hydride transfer from boron to carbon would give ethylborine, $EtBH_2$. Disproportionation would occur, producing first Et_2BH and then the final product triethylboron. An alternative route for forming triethylboron would be by reaction between the ethylborines and ethylene, again with hydride transfer.

Diborane is now easily prepared, and clearly as a method for preparing organoboron compounds, reaction between this hydride and the carbon–carbon π-bond is capable of wide variation because the hydrogen atoms of ethylene may be substituted by other atoms or groups. Treatment of diborane with these substituted ethylenes should afford hitherto unknown organoboron compounds, or compounds already known but obtained by other and sometimes more difficult methods.

This paper describes the effect on the borine–ethylene reaction of substituting ethylenic hydrogen by fluorine atoms.

1. EXPERIMENTAL

Purification and handling of materials

The tetrafluoroethylene supplied was reported as having no impurities, other than polymerization inhibitor, at concentrations greater than 10 p.p.m. After the inhibitor had been removed by chemical means, an analysis gave $M = 100{\cdot}2$. (Calc. for C_2F_4: M, 100·0; v.p. (vapour-pressure) 62·24 mm at −111·9°C (in reference 6, 62·27 mm). Purity of other fluorocarbons used in this work was similarly checked after distillation *in vacuo*: $CF_2{:}CH_2$ (Found: M, 63·8. Calc. for $C_2H_2F_2$: M, 64·02) v.p. 21·75 mm at −130°C. $CFH{:}CH_2$ (Found: M, 46·18. Calc. for C_2H_3F: M, 46·04) v.p. 43·65 mm at −111·9°C. $CF_2{:}CFH$ (Found: M, 82·04. Calc. for C_2HF_3: M, 82·03) v.p. 19·80 mm at −111·9°C. C_2H_3F (Found: M, 48·5. Calc. for C_2H_3F, M, 48·1) v.p. 195 mm at −63·5°C. The ethylene used had a v.p. of 453 mm at −111·9°C (in reference 7, 455 mm).

The diborane used had a v.p. 225·5 mm at −111·9°C (in reference 8, 225·0 mm).

All experiments were conducted using a high-vacuum system of conventional design. Vapour-pressure measurements on the ethylboron fluorides were made using a tensimeter.[9] All temperatures below 0°C were determined using vapour-pressure thermometers.

During the work here described extensive use was made of infra-red spectra as a means of qualitatively identifying constituents of gaseous mixtures. Spectra were recorded, using a Model 21 Perkin–Elmer double-beam spectrometer, and a 4 cm gas cell equipped with KBr windows.

Pure samples of the fluorocarbons, as well as mixtures of known composition, were used to calibrate the mass spectrometer employed in this work.

Microanalyses were made by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Gas non-condensable at the temperature of liquid nitrogen was collected in a gas burette by means of an automatic Sprengel pump. As this pump* has not been described in the chemical literature, yet is extremely useful, a brief description is given here. Pellets of mercury, spilling intermittently from the

* The apparatus in essentially this form had its origin in the laboratory of Professor BURG, where it was devised by R. I. WAGNER, F. G. A. STONE and A. B. BURG.

[3] D. T. HURD *J. Amer. chem. Soc.* **70**, 2053 (1948).
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[9] A. B. BURG and H. I. SCHLESINGER *J. Amer. chem. Soc.* **59**, 780 (1937).

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reservoir *A*, trap the gas present in *B* and carry it down the 3 mm bore capillary *C* into the gas burette *D*. In operation, the apparatus is filled with mercury up to line *E*. Mercury is lifted in neat pistons up the tube *F* by application of a rough vacuum at *G* and careful admission of air at *H*. Mercury is recycled through the valve *J*, a steel ball ground into place so as to permit the mercury to flow only downwards through this tube. When a length of recycled mercury appears above point *K*, it is lifted by the air to reservoir *A*, causing a like amount to spill into the capillary.

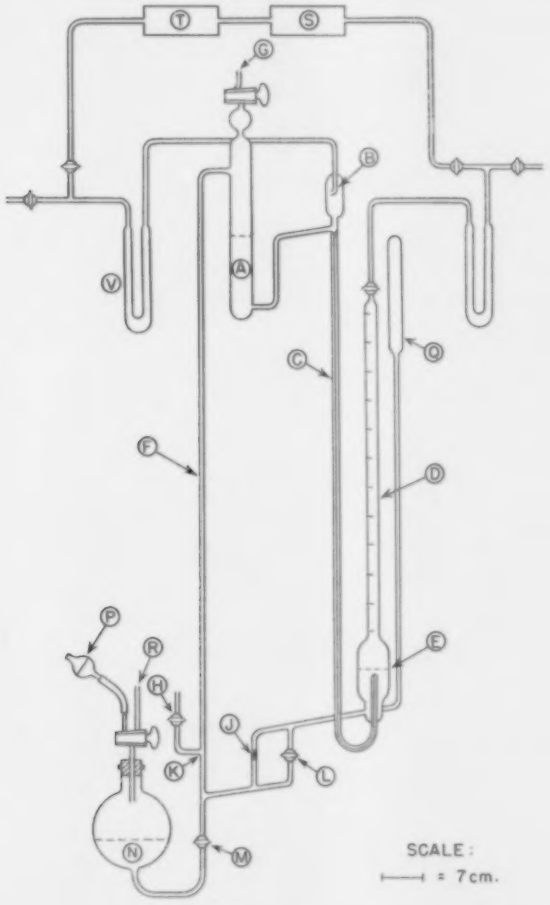

FIG. 1.—Automatic Sprengel pump.

When the gas has been quantitatively transferred to the gas burette, pumping is stopped by closing *H*. Stopcock *L* is opened to by-pass valve *J*, stopcock *M* is opened, and mercury from the main reservoir *N* flows into the apparatus. Additional pressure is exerted using bulb *P*. Rising mercury compresses the gas in the burette to one of the calibrated marks and also fills the arm *Q*, which has previously been highly evacuated, and now serves as the closed end of a manometer from which the gas pressure is read. Volume and temperature are noted and the gas volume calculated. Mercury is again lowered to the operating level by a rough vacuum at *R*.

Combustion of the gas is carried out by opening suitable stopcocks and using the pump to circulate the gas through the furnaces *S* (copper oxide at 750°C) and *T* (copper metal at 400°C). Water formed is removed by a −78·5°C bath at *V*. Other products are then collected in the burette and measured.

The reaction between boron hydride and tetrafluoroethylene

(a) *Choice of ratios of reactants.* During investigation of the effect of diborane on tetrafluoroethylene at 80–100°C it was found that if the B_2H_6:C_2F_4 molar ratio was 1 : 2, or the mixture even richer in B_2H_6 than this ratio, serious explosions occurred, but only after the reactants had been heated for some hours. Thus when 510 c.c.* B_2H_6 was heated with 1019 c.c. C_2F_4 at 80°C in a 1 l. Pyrex reaction-bulb the mixture exploded 20 hr later, completely destroying the oven used in the experiment. However, no explosions took place when diborane was heated with excess of tetrafluoroethylene, provided initial pressure in the reaction vessel was less than 1·5 atm. Furthermore, no explosions were ever encountered at room temperature even with B_2H_6:C_2F_4 ratios of 1 : 2 or more. It seemed, therefore, that at temperatures above 80°C, explosions were caused by the action of higher boranes on tetrafluoroethylene, since under conditions involving an excess of diborane there would be the likelihood of borine fragments reacting with themselves giving higher boranes. Then after some hours there would be a sufficient concentration of these higher boranes to react explosively with tetrafluoroethylene. To put this idea on a firmer basis, a 15·7 c.c. sample of C_2F_4 was added to 12·1 c.c. B_5H_9 in a glass tube of 30 ml capacity. The tube was sealed off from the vacuum line and allowed to remain at room temperature for an hour, during which time no change was visible. The tube was then placed in a steam-bath, where it exploded with sufficient force to remove the top of the bath.

(b) *Room-temperature reactions.* An experiment typical of many at room temperature is described here in detail in order to demonstrate how the products of other experiments mentioned in this paper were separated and identified. A 1 l. Pyrex bulb was filled with 960 c.c. C_2F_4 and 318 c.c. B_2H_6 (molar ratio B_2H_6 : C_2F_4, 1 : 3). After a few days a white solid began forming on the inside of the reaction bulb, but the latter was not reattached to the vacuum system until 33 weeks later, by which time all material containing boron–hydrogen bonds had been consumed by reaction with olefins. On opening the bulb, 15·5 c.c. H_2† was removed, and the other volatile products were separated by distillation *in vacuo*, giving well-defined fractions at −196°C(I), −130°C(II) and −96°C(III). The white solid remained in the bulb, since it was non-volatile at room temperature.

Fraction I (715 c.c.) was treated with water but no hydrogen was formed showing that all diborane had been used up in the reaction. The volume, however, was reduced to 370 c.c. (average *M*, 98·4; significantly lower than *M*, 100·0 calculated for C_2F_4). Mass spectrometer analysis of gas which survived water treatment gave: C_2F_4, 93·87; CF_2:CH_2, 3·95; C_2H_4, 0·22; C_2H_6, 0·11; CF_2:CFH, 0·04 mole per cent. There was little doubt that the gas absorbed by water was BF_3, since it was volatile enough to pass a U-trap at −130°C, yet no non-condensable gas was formed on hydrolysis. Quantitative analysis of the solution for fluoride[10] ion confirmed this (Found: F^- equivalent to 341 c.c. BF_3).

Analysis of II (243·8 c.c.) was more difficult. Previous experiments had shown that only the major part of these −130°C fractions reacted with trimethylamine. Thus they did not entirely consist of boron-containing material. This became obvious when it was found that after the −130°C fractions had been treated with an excess of trimethylamine giving a solid, the gas recovered did not have an infra-red spectrum identical with pure trimethylamine. Separation of mixture II into its constituents was accomplished, therefore, by treatment with excess of Me_3N (310·9 c.c.) to give a solid *addition compound* $Me_3\overset{+}{N}\cdot\overset{-}{B}EtF_2$, m.p. 23·9–25·3°C (Found: C, 43·66; H, 10·17; N, 10·50; B, 8·25; F, 27·87. $C_5H_{14}BF_2N$ requires: C, 43·84; H, 10·30; N, 10·23; B, 7·90; F, 27·74 per cent), and 106·1 c.c. gas. These volumes in themselves imply that II consisted of 224·3 c.c. $EtBF_2$ and 19·5 c.c. of other material. Confirmation was supplied by treating the recovered gas (106·1 c.c.), trimethylamine plus impurity, with BF_3 (126·1 c.c.) giving solid $Me_3\overset{+}{N}\cdot\overset{-}{B}F_3$, and 17·4 c.c. gas retained at −130°C. The excess of BF_3 (41·0 c.c.) was condensed at −196°C. This 17·4 c.c. "impurity" in the $EtBF_2$ appeared to consist principally of the *olefin* CFH:CFH (Found: *M*, 65·2; $C_2H_2F_2$ requires *M*, 64·0. When 4·01 c.c. were ignited over CuO at 800°C 8·43 c.c. CO_2 was produced. Expected: 8·02 c.c. CO_2. Mass spectrometer analysis showed the principal peak to be at $M/e = 64$, and the spectrum differed from all other fluoro-olefins used in this work) presumably as a mixture of *cis*- and *trans*-forms.

Fraction III (44·14 c.c. 247·5 mg) also proved to be a mixture, as did all the −96°C fractions

* Throughout this paper quantities of material expressed as c.c. refer to the s.t.p. volume.

† It is hardly necessary to point out that the small quantities of hydrogen formed in some of the reactions described in this paper came from the well-established tendency of diborane to decompose.

[10] R. J. ROWLEY and H. V. CHURCHILL *Industr. Engng. Chem. (Anal.)* **9**, 551 (1937).

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obtained from the many diborane–fluoroethylene reactions conducted at room temperature. Indeed, the small amounts of material prevented characterization of all components of these mixtures. In this particular experiment, III was distilled through a −78·5°C bath four times, giving fractions passing −78·5°C of volumes: 13·56 c.c. (*M*, 101·3), 9·8 c.c. (*M*, 105·4), 4·94 c.c. (*M*, 107), and 4·18 c.c. (*M*, 111). These fractions were combined (32·48 c.c.) and found to react with 32·49 c.c. Me_3N, when treated with an excess of this base, giving a liquid addition compound. Combination of that part of III passing a trap at −78·5°C with an exactly equal volume of Me_3N did at least imply the presence of 32·48 c.c. of boron. The remainder of III could be divided into a fraction retained at −46°C (3·5 c.c.), probably triethylboron, and a fraction at −78·5°C (8·16 c.c., *M*, 117). These two small fractions also combined in a 1 : 1 ratio with Me_3N.

Total boron content of III was thus 44·1 c.c. (i.e. only 7 per cent of the boron used in the reaction); the boron content of II, 224·3 c.c.; and the boron content of I, 345 c.c. Hence these volatile reaction products account for 613·4 c.c. of the 636 c.c. of boron taken as B_2H_6 for reaction. The remainder of the boron appeared in the white *polymer* (Found: C, 23·98, 24·01; H, 0·32, 0·00; F, 71·44, 70·25; B, 4·16, 6·88 per cent; *M*, isothermal method,[11] 650).

(c) *Reactions at* 80–100°C. In a representative experiment B_2H_6 (116·6 c.c.) was heated with C_2F_4 (438·4 c.c.) at 80°C for 24 hr in a 1 l. Pyrex bulb. White polymer appeared in the bulb within a few hours of starting the experiment. The reaction vessel was attached to the vacuum-line through a tube-opener, and 6·80 c.c. H_2 removed. The volatile products were then separated in a manner similar to that described under (b) above, giving 134 c.c. BF_3 (characterized as $Me_3\overset{+}{N}\cdot\overset{-}{B}F_3$) (Found: C, 28·11; H, 7·19; N, 10·89; $C_3H_9BF_3N$ requires C, 28·38; H, 7·15; N, 11·04 per cent) and 233·6 c.c. ethylenes (Mass spectrometer analysis: C_2F_4 95·37; CF_2:CH_2, 3·31; CHF:CH_2, 0·48; and CF_2:CFH, 0·17 mole per cent) at −196°C. The −130°C fraction consisted of 68·6 c.c. $EtBF_2$ (again separated as $Me_3\overset{+}{N}\cdot\overset{-}{B}F_2Et$) and 10·0 c.c. material inert towards Me_3N, probably CFH:CFH. The −96°C fraction consisted of only 22·3 c.c. material. The 22·3 c.c. fraction was treated with 41·6 c.c. Me_3N forming a liquid complex, 19·2 c.c. Me_3N being recovered. Treatment of the complex with excess of BF_3 in an attempt to form $Me_3\overset{+}{N}\cdot\overset{-}{B}F_3$ failed to displace all the Lewis acids combined with the Me_3N. However, 7·6 c.c. Et_2BF (identified by its infra-red spectrum) was obtained. It was apparent from this experiment as well as others involving diborane and tetrafluoroethylene that the −96°C fraction contained Lewis acids stronger than BF_3.

The polymer contained a little boron, although volatile products (equivalent to 225·0 c.c. boron) as usual accounted for the major portion. The diborane taken for reaction corresponded to 233·2 c.c. boron.

(d) *Some properties of the polymer*. The polymer proved to be interesting in that it was very soluble in a variety of donor solvents like ether, acetone, triethylamine, ethyl acetate and glacial acetic acid, but insoluble in benzene, carbon tetrachloride, carbon disulphide and chloroform. The molecular weight varied from reaction to reaction with a maximum *M*, 1183 (Found: C, 23.97; H, 0·33; B, 4·38; F, 71·00 per cent).

The reaction between diborane and vinyl fluoride

A 1 l. bulb containing 124·5 c.c. B_2H_6 and 636·0 c.c. CH_2:CHF was heated for 10 days at 55°C and then for 2 days at 70°C. The bulb was then opened and its contents examined. No hydrogen had been formed, indicating no loss of BH_3 by pyrolysis. Volatile material was fractionated through U-traps at −196°C (I), −130°C (II), and −96°C (III).

The infra-red spectrum of I (284·0 c.c.) indicated absence of B—H containing material. All B_2H_6 had, therefore, been consumed. This was confirmed when on treatment of I with water, no hydrogen was formed but the volume decreased to 258·5 c.c. (infra-red spectrum corresponded to vinyl fluoride with a trace of ethylene) owing to absorption of 25·5 c.c. BF_3 (indicated in spectrum of I before hydrolysis).

The infra-red spectrum of II (126·7 c.c.) also showed no B—H containing material, but showed the presence of a small quantity of CH_2:CHF. Refractionation of II through a trap at −130°C yielded 6·8 c.c. CH_2:CHF, and 119·9 c.c. of pure $EtBF_2$.

[11] R. SIGNER *Liebigs Ann.* **478**, 246 (1930). See STEYERMARK *Quantitative Organic Microanalysis*. Blakiston (1951).

Fraction III was distilled through a trap at −45°C, where 83·8 mg (19·1 c.c.) Et_3B (infra-red spectrum identical with triethylboron specimen prepared via Grignard reagent) was retained. An 81·4 c.c. sample Et_2BF (identified by infra-red spectrum) was recovered in the −96°C trap.

The various components of the mixture account for 245·9 c.c. boron, 99 per cent of the boron taken as diborane for reaction. No polymerization of vinyl fluoride was observed.

Several other reactions between B_2H_6 and CH_2:CHF were carried out under the same conditions of temperature and pressure, using slightly different reaction ratios. No difficulties were encountered. However, when 142·5 c.c. B_2H_6 and 571·5 c.c. CH_2:CHF were heated at 80°C, an explosion, without breakage of the bulb, occurred after a few hours. On opening the reaction vessel, the walls of which were entirely black, 1190 c.c. H_2 was removed, and 161·5 c.c. condensable gas recovered. This gas was identified as 143·0 c.c. BF_3, 4·8 c.c. B_2H_6, 1·0 c.c. CH_2:CHF and 3·0 c.c. $EtBF_2$. The black solid appeared to be a mixture of carbon, boron, and solid boron hydride.

The reaction between diborane and 1:1 *difluoroethylene*

In a typical experiment, CF_2:CH_2 (646·5 c.c.) and B_2H_6 (158·0 c.c.) were heated in a 1 l. Pyrex bulb at 50°C for 10 days, and then at 65°C for 4 days. On opening the bulb, no hydrogen gas was found. The reaction products were taken into the vacuum system and distilled through traps at −196°C (I), −130°C (II) and −96°C (III). Infra-red spectrum of I (506 c.c.) indicated it to be a mixture of BF_3 and fluoroethylenes. Treatment with water gave no hydrogen, but removed 138·0 c.c. BF_3, leaving 368 c.c. fluoroethylenes (Mass spectrometer analysis: CF_2:CH_2, 59·9; CFH:CH_2, 36·9; C_2H_4, 1·2; CFH:CFH, 1·42; CF_3, 0·2 mole per cent). Fraction II consisted of 115·1 c.c. $EtBF_2$, and III 62·1 c.c. Et_2BF. Both boron fluorides were identified by their spectra. No polymerization of CF_2:CH_2 had occurred, and boron in the volatile products accounts for 99·7 per cent of the boron taken as B_2H_6.

The reaction between diborane and trifluoroethylene

A mixture of CF_2:CFH (649·0 c.c.) and B_2H_6 (159·3 c.c.) was heated at 55°C for 10 days, and then at 65°C for 3 days. No hydrogen was formed. Infra-red analyses of the products showed absence of absorption bands corresponding to B—H. Products were identified as 290·4 c.c. fluoroethylenes (Mass spectrometer analysis: CF_2:CFH, 90·8, CF_2:CH_2, 8·3; CH_2:CHF, 0·2; C_2H_4, 0·1 mole per cent), 165·0 c.c. BF_3, 103·9 c.c. $EtBF_2$, 84·0 c.c. fluorocarbon (infra-red spectrum corresponding to the compound CFH:CFH) and 21·9 c.c. boron containing material condensed at −96°C (established as a mixture of Et_2BF and Lewis acids stronger than BF_3 by trimethylamine treatment).

The reaction between diborane and ethylene

In one experiment, C_2H_4 (662·0 c.c.) and B_2H_6 (150·5 c.c.) were heated in a 1 l. bulb at 60°C for 10 days. No hydrogen gas was formed, and no C_2H_4 or B_2H_6 were recovered. Pure Et_3B, 1·0634 g (243·0 c.c.) was condensed at −45°C. The only other product was $Et_3B_2H_4$, 24·85 c.c. (Found: *M*, 85·2; $Et_2B_2H_4$ requires *M*, 83·8. Infra-red spectrum different from any other observed in this work showed bands corresponding to B—H, B—C and C—H) condensed at −96°C.[12]

A mixture of C_2H_4 and B_2H_6 (molar ratio 4·4 : 1) heated under milder conditions again gave Et_3B as the main product, but a small quantity (3·7 c.c.) EtB_2H_5[12] (condensed at −130°C. Infra-red different from any other spectrum observed in this work, but nevertheless showed presence of B—C, B—H and C—H) was also isolated.

The effect of diborane on ethyl fluoride

A mixture of C_2H_5F (635·4 c.c.) and B_2H_6 (317·4 c.c.) was allowed to remain at room temperature for 11 months, by which time formation of solid boranes was observed. The reaction bulb was then opened, 102·4 c.c. H_2 removed, and gas condensable in liquid nitrogen examined. The mixture consisted of 262·3 c.c. B_2H_6, 623·7 c.c. C_2H_5F (identified by infra-red spectrum) corresponding to 98·4 per cent of this compound taken for reaction, and 5·1 c.c. B_5H_9 (identified by comparing the infra-red spectrum with that of a pure sample).

Other mixtures of diborane and ethyl fluoride also failed to react over periods of months at room temperature.

[12] H. I. SCHLESINGER, L. HORVITZ and A. B. BURG *J. Amer. chem. Soc.* **58**, 407 (1936).

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Synthesis of ethylboron fluorides from diborane, triethylboron and tetrafluoroethylene

(a) A mixture of B_2H_6 (156 c.c.), Et_3B (160·6 c.c.) and C_2F_4 (620·7 c.c.) was allowed to remain in a 1 l. bulb for a period of 1 year. During this time a quantity of white polymer formed, but in much smaller amount than when diborane and tetrafluoroethylene are alone mixed. After the bulb had been attached through a tube-opener to the vacuum line, 5·1 c.c. H_2 was removed. Other products were separated in the usual manner into 391·5 c.c. fluoroethylenes, 1·5 c.c. BF_3, 385 c.c. $EtBF_2$, 65·8 c.c. Et_2BF and 16·4 c.c. Et_3B. Infra-red spectrum of all fractions showed a complete absence of bands corresponding to B—H.

(b) After a mixture of B_2H_6 (145·8 c.c.), Et_3B (186·9 c.c.) and C_2F_4 (662 c.c.) had been heated at 55°C for 10 days the products were, BF_3 (68·2 c.c), fluoroethylenes (439 c.c.), $EtBF_2$ (251 c.c.), Et_2BF (58·1 c.c.) and Et_3B (88 c.c.). No H_2 or B—H-containing material was formed, but some polymer was observed in the reaction bulb.

Characterization and properties of ethylboron fluorides

For physical studies. $EtBF_2$ was readily liberated from its trimethylamine complex by treatment at room temperature with the stronger Lewis acid boron trifluoride. Thus a 226 c.c. sample of $\overset{+}{Me_3}N\cdot\overset{-}{B}EtF_2$, prepared by mixing equal volumes of Me_3N and $EtBF_2$ at −78·5°C, was treated with 246·0 c.c. BF_3. Liquid phase disappeared within an hour, and solid $\overset{+}{Me_3}N\cdot\overset{-}{B}F_2$ formed together with 224·8 c.c. ethylboron difluoride (Found: *M*, 78·3, 78·1; F, 20·1 per cent. $C_2H_5BF_2$ requires *M*, 77·9; F, 20·44 per cent) condensed at −130°C, and 20·3 c.c. BF_3 recovered at −196°C.

Vapour-pressures of $EtBF_2$ over the range −95°C to −45°C (Table 1) imply the relevant physical constants summarized in Table 4.

TABLE 1.—VAPOUR TENSIONS OF LIQUID $EtBF_2$

t, °C	−95	−83·6	−78·5	−63·5	−45·2
P_{mm} (found)	5·8	17·4	26·6	81·5	262
P_{mm} (calc.)	6·2	17·4	26·6	81·5	261·8

The compound Et_2BF (Found: *M*, 87·6; C, 55·3; H, 11·1 per cent. $C_4H_{10}BF$ requires *M*, 87·9: C, 54·7; H, 11·1 per cent) combined in a 1 : 1 ratio with trimethylamine forming a liquid adduct $\overset{+}{Me_2}N\cdot\overset{-}{B}FEt_2$ (Found: C, 55·9; H, 13·0; N, 9·9. $C_7H_{19}BFN$ requires C, 57·2; H, 13·03; N, 9·53 per cent).

Vapour-pressures of Et_2BF over the range −45°C to −13°C (Table 2) determine the relevant constants summarized in Table 4.

TABLE 2.—VAPOUR TENSIONS OF LIQUID Et_2BF

t, °C	−45·2	−35·6	−22·8	−16·0	−13·1
P_{mm} (found)	11·6	20·9	43·9	62·8	73·3
P_{mm} (calc.)	11·5	21·1	43·9	62·9	72·9

Stability of ethylboron difluoride, with respect to disproportionation into boron trifluoride and diethylboron fluoride, was examined by heating a 103·2 c.c. sample at 80°C for 48 hr. No decomposition occurred, and 102·8 c.c. $EtBF_2$ (identified from its molecular weight and infra-red spectrum) was recovered.

In a similar experiment, diethylboron fluoride was found to be thermally stable, showing no sign of disproportionation.

2. DISCUSSION

As described in the experimental section, the main boron-containing products formed on treating any of the fluoroethylenes with diborane are always boron trifluoride, ethylboron difluoride, diethylboron fluoride and triethylboron. Moreover, mass spectrometer analyses of tetra-, tri-, and 1-1-di: fluoroethylene residues recovered from the reactions of these olefins with diborane showed them to contain appreciable quantities of less fluorinated olefins.

These observations show that all the reactions follow an essentially similar course. Fluorine in the fluoroethylenes is first replaced by hydrogen derived from B—H-containing material. In this way ethylene is eventually formed, while at the same time B—F bonds are created. Once formed, the ethylene undergoes addition reactions with molecules containing B—H linkages, whereby B—C bonds are synthesized.

There are obviously a large number of possible reaction paths that can be followed during both replacement of fluorine by hydrogen from B—H, and addition of B—H to ethylene. Fortunately, the number of stable boron-containing molecules ultimately obtained is limited by the inherent tendency of unsymmetrical borine derivatives to disproportionate. A further limitation on the number of final products is imposed because several reaction intermediates react to give the same compounds. The probable reaction scheme is outlined on page 127.

Borine converts tetrafluoroethylene to trifluoroethylene, the BH_2F group being produced. The BH_2F molecule would be expected to exist as a dimer, and to be highly unstable, disproportionating to BH_3 and BHF_2. Fluoroborine could also attack tetrafluoroethylene or other fluoroethylenes, exchanging H for F, or alternatively it could add to ethylene giving EtB(H)F. The BHF_2 molecule would have similar properties, transferring hydride to carbon in the fluoroethylenes, and adding across the double bond in ethylene, giving $EtBF_2$. Disproportionation of BHF_2 would give another final product, boron trifluoride.

Under the proposed reaction scheme, attack of B—H on trifluoroethylene, formed from tetrafluoroethylene, would yield either 1:1-difluoroethylene or 1:2-difluoroethylene. 1:1-Difluoroethylene was indeed identified, by infra-red and mass spectrometer analysis, in the excess of tetra- or tri-fluoroethylene recovered at −196°C after reaction with diborane. 1:2-Difluoroethylene was not found in either the tetra- or the tri-fluoroethylene recovered from their respective reactions with diborane. Ethylboron difluoride condensing at −130°C, however, showed contamination with small quantities of a fluorocarbon which in the mass spectrometer gave a principal peak at $M/e = 64$, and had an infra-red spectrum corresponding to that expected for CFH : CFH. The compound CFH : CFH, presumably as a mixture of *cis*- and *trans*-isomers, would be expected to be less volatile than the other fluoroethylenes, and its appearance in the −130°C fractions rather than at −196°C is not unexpected. It is to be noted that *cis*- and *trans*-1:2-dichloroethylene are considerably less volatile than all other chloroethylenes.[13] The compound 1:2-difluoroethylene is of particular interest, since although it is a relatively simple molecule it has never been reported in the chemical literature. Unfortunately, it is formed in such small amounts by the reactions reported here that it has not been characterized completely, although it may be possible to do so at a later date.

Much other evidence for the proposed mechanism may be deduced from the work

[13] E. H. HUNTRESS *Organic Chlorine Compounds*. John Wiley, New York (1948).

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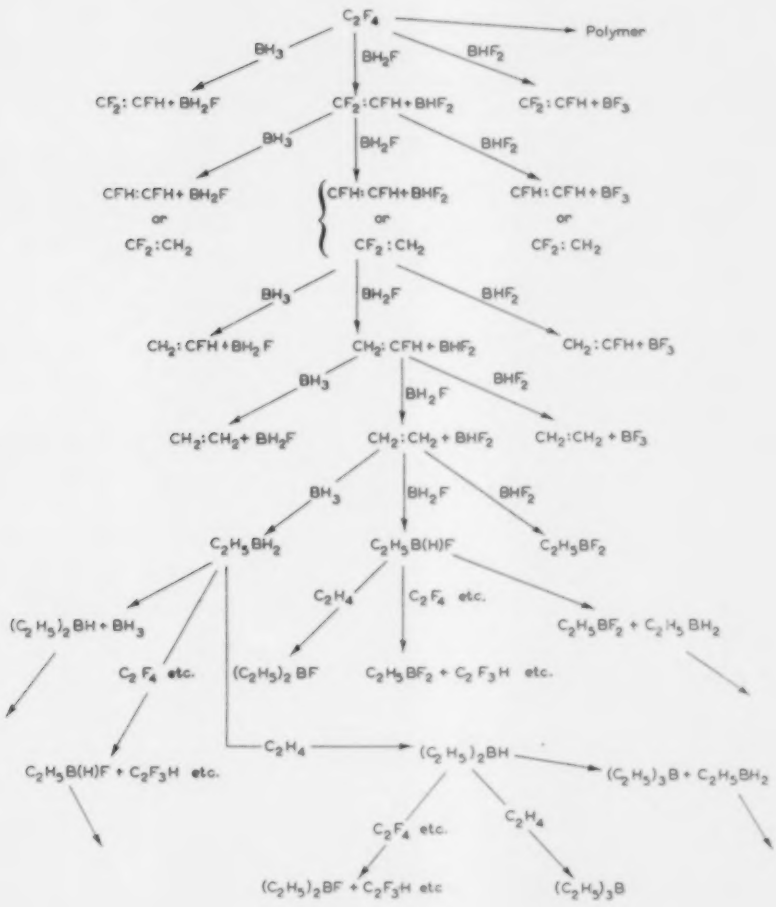

described in the experimental section. Thus, whereas the presence of ethyldiboranes as products of the diborane-ethylene reaction was not demonstrated in previous work,[3] these compounds were found under milder reaction conditions used by us. Moreover, in reactions carried out between diborane and fluoroethylenes at room temperature a very complex mixture of products was obtained whenever the reaction was stopped before all B—H-containing material was used up. One product, tentatively identified* as $EtB(H)F{\cdot}BH_3$, condensing in very small amounts at −96°C, could not be separated from diethylboron fluoride. Especially complicated were the mixtures obtained by treating vinyl fluoride with diborane at room temperature when small quantities of ethyldiboranes were detected. When reactions with vinyl fluoride were carried out

* Treatment of diethylboron fluoride and the impurity (infra-red showed B—H) believed to be $EtB(H)F{\cdot}BH_3$ with trimethylamine gave a liquid. Addition of boron trifluoride yielded Et_2BF, as expected, but also B_2H_6, and ethylboron difluoride. The latter would form by disproportionation of the EtB(H)F group.

above 50°C, however, boron trifluoride, ethyl- and diethyl-boron fluoride, and triethylboron were the only boron-containing compounds observed.

Distribution of boron among the products of diborane–fluoroethylene reactions varies with the ethylene used and is summarized in Table 3. With each olefin from experiment to experiment the boron distribution changes slightly even with a constant ratio of reactants. Nevertheless, this variation is small compared with the change in boron distribution brought about by substituting one fluoroethylene by another. Thus, with tetrafluoroethylene, molar ratio olefin : diborane of 4:1, yield is in the order $BF_3 > EtBF_2 \gg Et_2BF > Et_3B$. With vinyl fluoride it is $EtBF_2 > Et_2BF \gg BF_2 \sim Et_3B$. These changes in proportions of boron-containing products are to be expected under the reaction scheme suggested. Substitution of one fluoroethylene by another with a lower fluorine content should favour those reactions leading to B—C bond formation over those leading to B—F bond synthesis. Similarly, as indicated in Table 3, a change in ratio of reactants brings a slight but expected shift in boron distribution.

TABLE 3.—BORON DISTRIBUTION IN DIBORANE–FLUOROETHYLENE REACTIONS[a]

Olefin	Ratio of reactants olefin: B_2H_6	% Boron in the products as			
		BF_3	$EtBF_2$	Et_2BF	Et_3B
C_2F_4	4·2 : 1	58·0	30·0	0[b]	0[b, c]
C_2F_3H	4·1 : 1	51·7	32·6	0[b]	0[b, d]
1:1-$C_2F_2H_2$	4·1 : 1	43·6	36·5	19·7	0[e]
C_2FH_3	4·1 : 1	7·0	55·0	32·6	3·5
C_2F_4	3·1 : 1	54·2	35·3	0	0[b, c]
C_2FH_3	4·6 : 1	9·3	51·2	33·9	0

[a] Results presented in this Table refer to representative reactions conducted under conditions such that all B—H-containing material was consumed.
[b] Trace amounts of Et_2BF and Et_3B were sometimes obtained.
[c] In the B_2H_6/C_2F_4 reactions about 8 per cent boron taken as diborane for reaction is incorporated in the polymer, and a trace appears in the form of Lewis acids stronger than BF_3.
[d] Small amount of boron appears as acids stronger than BF_3.
[e] Small quantities Et_3B sometimes obtained.

A very large change in the proportions of products may be accomplished by a preliminary addition of triethylboron to the diborane–olefin mixture. Thus as described in the experimental section mixtures of diborane, triethylboron and tetrafluoroethylene give mainly ethyl- and diethyl-boron fluoride. Only a relatively small amount of boron appears as boron trifluoride. It is well known that addition of triethylboron to diborane quickly gives equilibrium mixtures of ethyldiboranes.[12] These can function as sources of ethylborines, $EtBH_2$ and Et_2BH. Obviously the latter are then fluorinated by the fluoroethylenes, giving $EtBF_2$ and Et_2BF as the main products.

During the course of this work there was very little evidence for addition of borines to fluoroethylenes, e.g.

$$CH_2{:}CHF + BH_3 \rightarrow (C_2H_4F)BH_2.$$

However, when tetrafluoroethylene or trifluoroethylene was treated with diborane,

boron-containing Lewis acids stronger than BF_3 were occasionally found, but in amounts far too small for identification. They may have been compounds with fluorine in the alkyl group. In any event, formation of these compounds was insignificant in comparison with the main reaction: conversion of fluoroethylenes to ethylene, followed by addition reactions of various borines occurring with ethylene only.

Whereas fluoroethylenes undergo complete reaction with diborane even at room temperature over a period of months, no reaction occurred between diborane and ethyl fluoride under the same conditions. This suggests that interaction of the borine group with the π-electrons of the double bond is a necessary part of the fluoroethylene–diborane reaction mechanism. It is possible, however, that ethyl fluoride and diborane would react at elevated temperatures under pressure, just as diborane and the paraffins react under such conditions.[3]

The compounds ethylboron difluoride and diethylboron fluoride are new. Some of their physical properties are summarized in Table 4. Like the methylboron fluorides[14] they do not disproportionate.

TABLE 4.—PHYSICAL PROPERTIES OF THE ETHYLBORON FLUORIDES

	m.p.[a] (°C)	b.p.[b] (°C)	Log P mm $= -A/T + B$		$\Delta H_{(vap)}$ (kcal mole^{-1})	Trouton's constant (cal deg^{-1} mole^{-1})
			A	B		
$C_2H_5BF_2$	−101·0	−25·4	1325	8·229	6·06	24·5
$(C_2H_5)_2BF$	−121·5	43·6	1479	7·550	6·77	21·4

[a] Stock magnetic plunger method.
[b] By extrapolation of vapour-pressure equation.

Acknowledgements—It is a pleasure to acknowledge support of this work by the William F. Milton Fund of Harvard University, especially for the award of a post-doctoral research fellowship to one of the authors (B. B.). We wish to thank the Freon Products Division of the E. I. du Pont de Nemours Company for supplying us with vinyl fluoride and trifluoroethylene.

[14] A. B. BURG *J. Amer. chem. Soc.* **62**, 2228 (1940).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 130 to 133. Pergamon Press Ltd., London

IRON(III)NITRILOTRIETHOXIDE

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Abstract—A suspension in methanol of ammonium tetrachloroferrate(III) and nitrilotriethanol hydrochloride reacts with ammonia to give ammonium chloride and a solution of iron(III)nitrilotriethoxide. On addition of ether, greenish-yellow hexagonal crystals of the monohydrate precipitate. Evaporation on the steam-bath of the solution of the hydrate leads to a greyish-white amorphous precipitate of anhydrous iron(III)nitrilotriethoxide. The possible structures of the two new compounds are discussed.

DUFF and STEER[1] reported that the addition to nitrilotriethanol to ferric chloride or hydroxide yielded no definite compound. In an attempt to prepare iron(III)nitrilotriethoxide, the reaction was studied again under conditions in which it might take the following course:

$$FeCl_3 + (HOC_2H_4)_3N + 3NaOH \rightarrow Fe(OC_2H_4)_3N + 3NaCl + 3H_2O$$

Excess nitrilotriethanol, glycol or *n*-butanol served as reaction media at temperatures up to 100°C. A red soluble complex, probably containing hydroxyl, formed at first. With increasing reaction time and temperature it changed partly to a yellow soluble complex. The reaction could not be completed without both soluble complexes yielding a whitish insoluble residue. Separation of the red and the yellow components from each other and of the insoluble residue from sodium chloride was difficult.[2] Further experiments indicated that iron(III)nitrilotriethoxide is better prepared at low temperature and avoiding water as side product by using ammonia as proton acceptor. A patent[3] coming to the author's attention after successfully using this method claims it to be generally applicable for preparing alkoxide solutions:

$$Fe^{+3} + 3HOR + 3NH_3 \rightarrow Fe(OR)_3 + 3NH_4^+$$

EXPERIMENTAL

Materials

The starting materials were of analytical reagent purity, except for the nitrilotriethanol, which was technical.

Preparations

(a) Ammonium tetrachloroferrate(III)[4] was prepared by melting 54·1 g (0·2 mole) of ferric chloride hexahydrate on a sandbath and adding 10·7 g (0·2 mole) of finely ground ammonium chloride. The mixture was stirred until it had turned from red over orange to olive. The residue was ground, dried overnight in the oven at 100°C, and kept in a desiccator. This crude product is less hygroscopic than anhydrous ferric chloride.

(b) Nitrilotriethanol is easily separated from other amino alcohols present in the technical product by precipitation of the hydrochloride.[5] 149·2 g of nitrilotriethanol in 150 ml of ethanol (95 per cent)

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[1] J. C. DUFF and E. H. STEER *J. chem. Soc.* (1932) 2861.
[2] J. B. MILNE Thesis (B.A.), University of British Columbia, Vancouver, B.C., Canada.
[3] FARBENFABRIKEN BAYER *Brit. Pat.* 695421; *Chem. Abstr.* **48**, 10049 (1954).
[4] K. HACHMEISTER *Z. anorg. Chem.* **109**, 179 (1920).
[5] J. H. JONES *J. Ass. off. Agric. Chem.* **27**, 467 (1944).

was added slowly under stirring to a mixture of 85 ml of concentrated hydrochloric acid with 100 ml of ethanol (95 per cent). After crystallization was completed, the crystals were separated by suction and left to dry at room temperature. 161·6 g were obtained, the yield being 87·0 per cent. Unlike the free base, the hydrochloride is not hygroscopic.

(c) Iron(III)nitrilotriethoxide hydrate. The crude ammonium tetrachloroferrate(III) (0·2 mole) was introduced into a 1000 ml flask equipped with a reflux condenser and containing 200 ml of absolute methanol. 37·1 g (0·2 mole) of nitrilotriethanol hydrochloride was added and the mixture saturated with ammonia gas dried over sodium hydroxide. The colour changed from red over orange to yellow. An intermediate precipitate dissolved until only ammonium chloride remained:

$$NH_4FeCl_4 + (HOC_2H_4)_3N{\cdot}HCl + 4NH_3 \rightarrow Fe(OC_2H_4)_3N + 5NH_4Cl$$

The flask was almost filled with benzene. After shaking, the ammonium chloride was allowed to settle and then separated by suction. Excess ammonia and a small amount of the methanol–benzene mixture was removed by distillation. The solution was repeatedly shaken with powdered silver carbonate until free of chloride. It was then treated with charcoal to remove silver ion. Anhydrous ether was added until crystallization began. The crystals were left to settle, separated by suction and dried at room temperature. 42·1 g were obtained, the yield being 95·7 per cent.

The compound was recrystallized in small portions by suspending it in benzene and adding dropwise just enough methanol to dissolve it. On slow addition of anhydrous ether, a little of the compound precipitated, carrying impurities which were centrifuged off. The centrifugate was carefully covered with anhydrous ether in a 70 ml test-tube. At the boundary, crystals formed after several hours. Crystallization was continued by mixing the two liquid layers with a glass rod. Small hexagonal greenish-yellow crystals formed. When heated slowly, the compound was decomposed without melting. It was very soluble in methanol and ethanol, soluble in higher alcohols, chloroform, and pyridine, but insoluble in ether, benzene, dioxane, acetone, and carbon tetrachloride. Water precipitated ferric hydroxide.

(d) Iron(III)nitrilotriethoxide. The hydrate (2 g) was dissolved in 30 ml of a mixture of methanol and dioxane (1 : 1) warming it slightly. The solution was filtered and evaporated on the steam-bath. The residue was washed with the solvent mixture and centrifuged. Washing and centrifuging were repeated until the wash-liquid remained colourless. After washing with anhydrous ether, the iron(III)nitrilotriethoxide was dried in a vacuum desiccator. A 71 per cent yield (1·3 g) was obtained. The centrifugates were combined and evaporated to dryness. An additional quantity of the compound was obtained as a grey-white powder in this manner. When heated slowly it was decomposed without melting. It was insoluble in organic solvents. Water hydrolysed to ferric hydroxide.

(e) Iron(III)nitrilotriethoxide hydrate was obtained in 77 per cent yield by the method described under (c), but with ethanol as solvent.

(f) Iron(III)nitrilotriethoxide was prepared by evaporating on the steam-bath the ethanol solution of the hydrate obtained by method (e) and washing the residue with absolute ethanol.

Analysis

Microanalyses were carried out by Mr. Alfred Bernhardt, Mikroanalytisches Laboratorium, Max Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany.

RESULTS

The crystals precipitated from cold methanol or ethanol have the composition of the monohydrate and not of the corresponding alcoholates of iron(III)nitrilotriethoxide. Though anhydrous starting materials were used, the atmosphere had access to the solution. The basic compound must have taken up water instead of the more weakly acidic solvents.

The hydrates from either methanol or ethanol are dehydrated on the steam-bath, as the composition of the products obtained is that of anhydrous iron(III)nitrilotriethoxide.

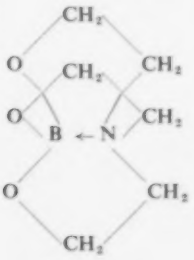
TABLE 1.—PERCENTAGE COMPOSITION OF COMPOUNDS DEPENDING ON METHODS OF PREPARATION

	C	H	N	O	Fe
Precipitated from cold methanol (c)	32·82	6·81	6·38	28·65	24·90
Precipitated from cold ethanol (e)	32·99	6·64	6·47	29·36	24·43
Calculated for $Fe(OC_2H_4)_3N$, H_2O	32·76	6·42	6·37	29·09	25·39
Obtained from hot dioxane–methanol (d)	35·20	6·14	6·97	24·15	27·87
Obtained from hot ethanol (f)	35·40	6·23	7·25	24·08	27·04*
Calculated for $Fe(OC_2H_4)_3N$	35·68	5·99	6·94	23·77	27·66

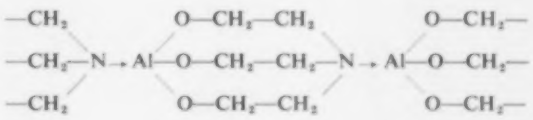
* Calculated as difference and not determined as Fe_2O_3 because of loss of substance.

DISCUSSION

Nitrilotriethoxides of the trivalent elements boron,[6–8] aluminium[9] and bismuth[10] have been prepared and the following chelate structures discussed:



I



II

BROWN and FLETCHER[7] and HEIN and BURKHARDT[8] assigned the five-membered ring structure I to nitrilotriethyl borate. It is unlikely for iron(III)nitrilotriethoxide. Co-ordinate covalent bonds between iron and amino nitrogen generally do not form if co-ordination with oxygen is possible. Structure I can also not explain the tendency for hydration.

HEIN and ALBERT[9] regarded the anhydrous aluminium compound as a polymer of units with eight-membered rings (structure II). A molecular model predicts little strain for such rings in iron(III)nitrilotriethoxide. In the hydrate the water molecules

[6] C. A. ROJAHN *Ger. Pat.* 582149; *Chem. Abstr.* **27**, 5153 (1933).
[7] H. C. BROWN and E. A. FLETCHER *J. Amer. chem. Soc.* **73**, 2808 (1951).
[8] F. HEIN and R. BURKHARDT *Z. anorg. Chem.* **268**, 159 (1952).
[9] F. HEIN and P. W. ALBERT *Z. anorg. Chem.* **269**, 67 (1952).
[10] W. T. MILLER *J. Amer. chem. Soc.* **62**, 2707 (1940).

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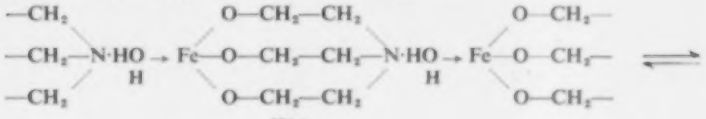
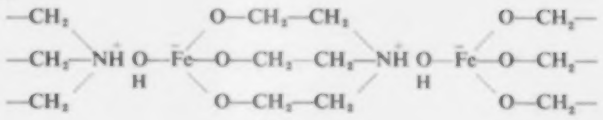
presumably bridge the iron and nitrogen atoms:



II(a)



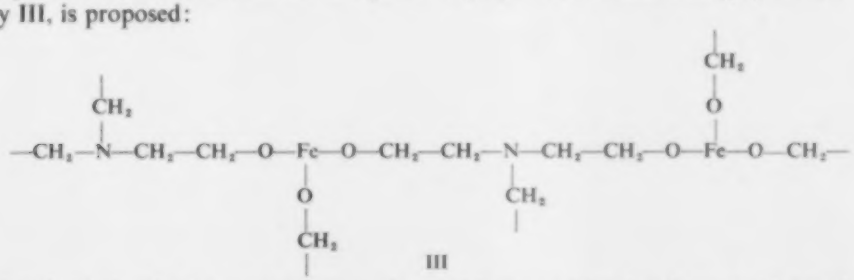
II(b)

It would depend on the relative distance of the proton from either oxygen or nitrogen whether the crystals consist essentially of molecules with hydrogen bonding or of zwitterions.

A comparison with related compounds makes a hydroxo complex plausible. MEERWEIN and BERSIN[11] found iron triethoxide to add an ethoxo group forming negative tetraethoxoferrate(III) ions. They also prepared a monohydroxo triethoxo complex of aluminium. BRINTZINGER and HESSE[12] obtained yellow iron(III)nitrilotriacetate as the monohydrate. They accepted a structure analogous to II(a), admitting that it does not explain the fact that the water is not given up even at 170°C. They did not conclude that it may be bound ionically, as in II(b).

Iron(III)nitrilotriethoxide hydrate hydrolyses more slowly to ferric hydroxide than iron triethoxide. If structure II(b) is correct, the compound is already partly hydrolysed. The relative stability to further attack could be due to chelation.

Upon dehydration, the yellow iron(III)nitrilotriethoxide hydrate becomes white and the solubility at room temperature is lost. The removal of water from the proposed structure of the hydrate leads to a structure analogous to II for the anhydrous compound. One would expect such a compound to dissolve in cold alcohol, the weak bond to amino nitrogen being replaced by a co-ordinate bond to the oxygen of the solvent. However, it takes boiling temperatures of solvents such as *n*-butanol (b.p. 117·7°C) to redissolve the complex. A polymeric structure, roughly indicated by III, is proposed:



III

The dissolution in hot excess *n*-butanol would be caused by depolymerization under rearrangement of the chelate rings.

Acknowledgments—The author gratefully acknowledges the financial support of the President's Committee on Research at the University of British Columbia. He would also like to thank JOHN B. MILNE for his help in carrying out the preliminary experiments.

[11] H. MEERWEIN and T. BERSIN *Liebigs Ann.* **476,** 113 (1929).
[12] H. BRINTZINGER and G. HESSE *Z. anorg. Chem.* **249,** 299 (1942).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 134 to 137. Pergamon Press Ltd., London

THE REACTION OF ALUMINIUM BOROHYDRIDE WITH TIN AND LEAD TETRAMETHYL

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(*Received* 8 *May* 1957)

Abstract—Tin and lead tetramethyl do not react with diborane but both react vigorously with aluminium borohydride giving solid products which decompose ultimately to tin or lead, hydrogen, methylated boranes and methyl aluminium borohydride, $MeAl(BH_4)_2$. No dimethyl aluminium borohydride or trimethyl aluminium are found. The nature of the decomposition products suggests the intermediate formation of compounds such as $Me_2Sn(BH_4)_2$ and Me_3PbBH_4, but there is no evidence for replacement of more than two methyls by borohydride groups. Possible explanations are given for the limitations observed in the replacement of borohydride by methyl groups, and vice versa.

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BOROHYDRIDES of several metals have been prepared by various methods, e.g. by the reaction of the metal hydride or alkyl with diborane[1,2] or by metathetic reactions, involving a metal alkyl[3] or other metal compound[4,5] and another borohydride, usually that of lithium or aluminium. The object of the present work was to investigate the possibility of preparing covalent borohydrides of tin and lead by the reaction of either diborane or aluminium borohydride on the appropriate tetra-alkyl compound—the latter being chosen, since they are typical tetracovalent compounds and the alkyl groups are known to be replaceable by a wide variety of other groups.

EXPERIMENTAL

All manipulations were carried out in a Stock-type vacuum apparatus as described by SANDERSON.[6] Aluminium borohydride was prepared (1) by the reaction of equimolar amounts of lithium aluminium hydride and boron trichloride in ether;[7] the aluminium borohydride was displaced from its etherate by treatment with aluminium chloride in benzene and then fractionated until pure (v.p. at 20°C = 286 mm). (2) By heating together solid aluminium chloride and a mixture of potassium borohydride and lithium chloride, essentially the method of SCHLESINGER and BROWN,[5] who found that lithium borohydride gave better yields by this method than did sodium or potassium borohydride—hence the addition of lithium chloride in the present procedure. The yield by this method was about 50 per cent, together with some diborane. The latter was more conveniently prepared by reduction of boron trichloride in ether by lithium aluminium hydride.[8] Tin and lead tetramethyl were prepared from the appropriate chloride and Grignard reagent, and fractionated in the vacuum apparatus until pure. Stannane was prepared by reduction of stannic chloride by ethereal lithium aluminium hydride.

In an experiment, measured amounts of each reactant were condensed together in a tube at liquid-nitrogen temperature; the tube was sealed and reaction allowed to proceed under particular conditions of time and temperature. The tube was then cooled again and opened to the vacuum system, when any non-condensable gas was taken off, identified and measured, using a Töpler pump,

[1] H. I. SCHLESINGER and H. C. BROWN *J. Amer. chem. Soc.* **75,** 199 (1953)
[2] H. I. SCHLESINGER, R. T. SANDERSON and A. B. BURG *J. Amer. chem. Soc.* **62,** 3425 (1940).
[3] H. I. SCHLESINGER, R. T. SANDERSON and A. B. BURG *J. Amer. chem. Soc.* **62,** 3421 (1940).
[4] H. R. HOEKSTRA and J. J. KATZ *J. Amer. chem. Soc.* **71,** 2488 (1949).
[5] H. I. SCHLESINGER and H. C. BROWN *J. Amer. chem. Soc.* **75,** 209, 222 (1953).
[6] R. T. SANDERSON *Vacuum Manipulation of Volatile Compounds.* John Wiley, New York (1948).
[7] H. I. SCHLESINGER and A. E. FINHOLT *Hydrides and Borohydrides of Light Elements.* NRL Report No. C-3147 (1947).
[8] A. E. FINHOLT, A. C. BOND and H. I. SCHLESINGER *J. Amer. chem. Soc.* **69,** 1199 (1947).

gas burette and combustion tube for this purpose. Excess of either reactant was then removed at the lowest possible temperature, and then the temperature was raised and volatile materials taken off, fractionated and analysed, as follows:

Methyl aluminium borohydride was identified (1) by its v.p.–temperature curve[7] and (2) by hydrolysis, yielding aluminium (as hydroxide), methane and hydrogen in the ratio 1 : 1 : 8 as required by the equation:

$$MeAl(BH_4)_2 + 9H_2O = CH_4 + 8H_2 + Al(OH)_3 + B(OH)_3$$

Diborane, and mixtures of diborane and methylated boranes $(BH_{3-x}Me_x)_2$, including trimethyl boron, were determined by (1) hydrolysis, giving the B : H ratio and (2) reaction with excess trimethylamine,[8] the trimethylamine taken up being equivalent to the boron (e.g. $B_2H_4Me_2 + 2Me_3N = 2Me_3\overset{+}{N}\cdot\overset{-}{B}H_2Me$). The results of (1) and (2) together then gave the mean composition of the mixture, i.e. the mean value of x in $(BH_{3-x}Me_x)_2$.

Non-volatile materials were analysed by thermal decomposition or hydrolysis followed by measurement of volatile or gaseous products as described above; the residues were finally analysed for aluminium and boron, and tin or lead, as appropriate.

RESULTS AND DISCUSSION

Diborane did not react with tin or lead tetramethyl, nor with stannane. However, aluminium borohydride reacted vigorously on warming excess of it with either tetramethyl compound from −190°C to ordinary temperature, forming a white solid which darkened rapidly. By more cautious warming, unreacted aluminium borohydride could be removed at −60°C, together with a little hydrogen; the reaction ratio $Al(BH_4)_3/M\,Me_4$ (M = Pb, Sn) varied between 1 : 1 and 2 : 1, though approaching the latter figure more closely with tin tetramethyl.

On warming further to −20°C, the lead reaction yielded a volatile fraction containing lead; this was removed, but decomposed rapidly, giving lead, methylated boranes, hydrogen, and the substance methyl aluminium borohydride, $MeAl(BH_4)_2$. No further separation of volatile material could be effected from the original reaction mixture, because it decomposed rapidly above −20°C, yielding similar products to those obtained from the volatile fraction. Tin tetramethyl reacted similarly, again yielding methyl aluminium borohydride, hydrogen, methylated boranes and tin. Under all the conditions of reaction investigated, varying temperature, reaction time and reactant ratio, no products other than these were obtained.

In particular, the following were sought for, but never found as such: dimethyl aluminium borohydride, trimethyl aluminium, hydrocarbons and borohydrides of tin and lead.

The absence of dimethyl aluminium borohydride, Me_2AlBH_4, is not surprising; it is known to be unstable, decomposing very easily to give boron trimethyl as a product, indicating a transfer of methyl groups from aluminium to boron. It is therefore plausible to suppose that the methylated boranes found in the present experiments were formed from the decomposition of compounds such as $Me_yPb(BH_4)_{4-y}$, or $Me_yPb(BH_3Me)_{4-y}$. In several experiments it was in fact found that in the volatile tin-containing fraction the ultimate products (other than methyl aluminium borohydride) were Sn, $B_2H_4Me_2$ and H_2, in the ratio 1 : 1 : 2, suggesting

$$Me_2Sn(BH_4)_2 = Sn + B_2H_4Me_2 + 2H_2$$

Dimethyl tin borohydride might then originate by a reaction

$$2Al(BH_4)_3 + SnMe_4 = Me_2Sn(BH_4)_2 + MeAl(BH_4)_2,$$

[8] H. I. Schlesinger, N. W. Flodin and A. B. Burg *J. Amer. chem. Soc.* **61**, 1078 (1939).

i.e. a 2 : 1 reactant ratio, as found. In some of the lead tetramethyl experiments, a similar Pb : $B_2H_4Me_2$: H_2 ratio indicated that the volatile lead compound might be $Me_2Pb(BH_4)_2$. In one experiment where the reaction time was very short, the products of decomposition of the volatile lead-containing fraction were Pb : BMe_3 : $2H_2$, suggesting Me_3PbBH_4, trimethyl lead borohydride. In other experiments, the decomposition product ratios did not correspond to any one methyl lead borohydride, and it is probable that here a mixture (e.g. $Me_2Pb(BH_4)_2$ + $Me_2Pb(BH_3Me)_2$) was formed. Moreover, it is significant that in all the reactions, methyl aluminium borohydride, which would be expected to distil off with unchanged aluminium borohydride, at −60°C, did not appear until the temperature was raised to between −30 and −20°C. This suggests that the white solid originally formed was made up of compounds containing both lead (or tin) and aluminium, and that these then decomposed to give methyl aluminium borohydride and methyl-lead (tin)-borohydride compounds of the kind suggested above.

One further fact is important. After separation of all the methyl aluminium borohydride from the reaction products, the Pb/B or Sn/B ratio in the remainder was never greater than 2. This clearly indicates that the unstable methyl lead or tin borohydrides formed never contained more than two BH_4 (or BH_3Me) groups in the molecule—there was no evidence at all for the formation of (e.g.) $MePb(BH_4)_3$ or $Pb(BH_4)_4$.

It is necessary therefore to explain why one, but not two, borohydride groups in aluminium borohydride can be replaced by methyl groups without loss of stability (with respect to decomposition) and without the appearance of dimerized molecules (methyl aluminium borohydride is monomeric[7]): and also why not more than two methyl groups can be replaced by BH_4 (or BH_3Me) groups in tetramethyl tin or lead, any such replacement producing an unstable compound. The nature of the metal-borohydride bond in covalent borohydrides has been considered only in the case of aluminium borohydride. Analysis of the infra-red spectrum of the latter agrees with a hydrogen bridge model for the structure in which the six bridge hydrogen atoms are at the vertices of a trigonal prism rather than at the vertices of an octahedron.[10] Longuet-Higgins,[11] using the trigonal model, suggested that there are three trigonal Al—B σ-bonds formed from the sp^2 hybrid orbitals of the aluminium and boron. Three π-bonds can then be formed by overlap of the three hybrid pd^2 orbitals of the aluminium with the remaining p-orbitals of the boron atoms, the bridge protons being situated at the antinodes of these bonds. Using this concept of the structure, the replacement of one borohydride by a methyl group can be considered. If the new Al—C σ-bond is formed by combination of an aluminium sp^2 with a carbon sp^3 hybrid orbital, no rearrangement of the remaining Al—B σ-bonds is required. Two π-bonds may then be formed from two pd hybrid orbitals of the aluminium and the p-orbitals of the boron atoms. If overlap is sufficiently good here, then the stability of the Al—B bonds may be comparable with those in aluminium borohydride itself; moreover, no dimerization is expected, since the aluminium has no suitable orbital available. Replacement of a second borohydride group to give dimethyl aluminium borohydride, with the Al—C and Al—B σ-bonds formed as before, requires that the single π-bond be formed by overlap of a p-orbital of

[10] W. C. Price *J. chem. Phys.* **17**, 1044 (1949).
[11] H. C. Longuet-Higgins *J. chem. Soc.* 141 (1946).

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aluminium with a similar *p*-orbital of boron, i.e. a p_π—p_π bond. Although this type of bond may occur in diborane, in this case the greater aluminium–boron distance is likely to preclude strong overlap, and this may explain the instability of dimethyl aluminium borohydride and its ready decomposition with rupture of both Al—B and B—H bonds. Moreover, if complete conversion of aluminium borohydride to trimethyl aluminium (or more correctly, to Al_2Me_6) is considered, the aluminium orbitals must rearrange and assume sp^3 hybridization. At the temperature used in the present experiments it is quite likely that this conversion would be extremely slow, in view of the energy required for rearrangement—hence the absence of trimethyl aluminium in the reaction products.

In tin and lead tetramethyl, the metal–carbon bonds are formed from sp^3 hybrid orbitals from each atom, and since the inner *d*-levels are fully occupied in the tin or lead, further increase in covalency is difficult. However, with σ-bonds from sp^3 hybrid atomic orbitals, weak π-bonding is possible using d^2 hybrid orbitals, giving two angular π-bonds. It is possible that the outer orbitals of tin or lead can be used in this way, in compounds such as $Me_2Sn(BH_4)_2$; if so, the maximum number of possible π-bonds is two, thereby restricting replacement of methyl by borohydride groups, as already noted. This is in contrast to the ability of some group IV*a* elements (e.g. Zr, Hf) to form tetra-covalent borohydrides $M(BH_4)_4$; but here the metal–boron σ-bonds may be formed by hybridization of *s*, *p* and *d* atomic orbitals, and low-energy *d*-orbitals are also available for π-bond formation.

These arguments are, in the absence of much structural evidence, necessarily speculative; in particular, further information regarding the structure of methyl aluminium borohydride would be welcome.

Acknowledgements—One of us (W. J.) thanks the Department of Scientific and Industrial Research for a grant.

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THE COMBUSTION OF ZIRCONIUM IN OXYGEN

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Abstract—The combustion of zirconium in oxygen leads to one of the highest temperatures obtainable by the combustion of metals. This temperature has been estimated from available thermodynamic data to be 4930°K at 1·0 atm pressure. A technique has been developed which enables a powdered zirconium–oxygen flame to be operated, thus producing the highest metal flame temperature reported to date.

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IN a recent publication[1] discussing some of the thermodynamic aspects of metal combustion, it was pointed out that a metal will burn in oxygen to produce a very high temperature if the reaction is rapid; the metal has a high heat of combustion; and the metallic oxide (combustion product) is thermally stable. (The requirement that the heat capacity of the oxide be low is usually of negligible significance.)

The discussion also pointed out that although it is not possible to predict with any accuracy which metal will produce the highest temperature during combustion, it would seem that this distinction belongs either to lanthanum, zirconium, hafnium or thorium. It is interesting to note that these are not the metals with the highest heats of combustion (see Table 1), which emphasizes the statement made above, that the heat of combustion is not the only criterion in determining combustion temperatures of metals.

TABLE 1.—HEATS OF COMBUSTION OF SOME METALS

Metal	Heat of combustion (kcal/g)
Al	7·43
Mg	5·9
Th	1·26
Zr	2·87
Hf	1·49
La	1·57
B	14·1
Be	16·3

The extreme reactivity of finely divided zirconium powder was observed, among others, by HARTMANN, NAGY and JACOBSON[2] when clouds of the metal ignited at room temperature when dispersed in air. However, an accurate value for the ignition temperature of bulk zirconium has never been reported. From statements made by

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[1] J. B. CONWAY and A. V. GROSSE Powdered Metal Flames. *Third Technical Report* High Temperature Project, Research Institute of Temple University. Contract N9-onr-87301. 1 August 1953.

[2] I. HARTMANN, J. NAGY and M. JACOBSON *Bureau of Mines Report of Investigation* 4835. December 1951.

MELLOR,[3] it would seem that the ignition temperature is about 1000°C. This is in fair agreement with the approximate value of 900°C indicated in the work of CUBICCIOTTI.[4] In any case, it seems certain that zirconium belongs to that class of metals in which the ignition temperature is below the melting point.[5]

THERMODYNAMIC CONSIDERATIONS

The calculation of the flame temperature obtained in the combustion of zirconium requires that certain thermodynamic data be available for the metallic oxide. These data include heat of formation, heat capacity of the solid and liquid phases, melting point, heat of fusion, boiling point, heat of vaporization and heat capacity of the gaseous oxide (the data for ZrO_2 together with their sources are given in Table 2). In addition, the thermal stability of the oxide must be considered by analysing free-energy data, and some knowledge of the vaporization process, i.e. whether the oxide vaporizes undissociated or by dissociation into atoms, must be available.

TABLE 2.—THERMODYNAMIC PROPERTIES OF ZrO_2

Heat of formation at 298°K, cal/mole	= 261,800[7]
Melting point, °K	2960[7]
Heat of fusion, cal/mole	20,800[8]
Boiling point, °K	4570[6]
Heat of vaporization at 2960°K, cal/mole	113,300[9]
Heat capacity, cal/moledegK	
Solid $C_p = 17{\cdot}80 - 4{\cdot}0 \times 10^5\, T^{-2}$[10]	
Liquid $C_p = 20$ (estimated)	
Gas $C_p = 10^8$	
Vapour-pressure of solid from 2014 to 2290°K	
$\log P(\text{atm}) = \dfrac{-34{\cdot}383}{T} - 7{\cdot}98 \times 10^{-4}\, T + 11{\cdot}98$[9]	
although very different data have been reported.[11]	

The atmospheric boiling point of zirconium dioxide has not been accurately determined. The preliminary value of 4570°K reported by MOTT[6] is considered to be too low,[1] since it was determined in a carbon system. Recent data for the vapour pressure of solid zirconium dioxide have appeared,[9,11] from which estimates of the atmospheric boiling point can be made to compare with the value reported by MOTT. These data are reproduced in Fig. 1, in which it is seen that the data of HOCH, NAKATA and JOHNSTON[9] are much higher than those of CHUPKA, BERKOWITZ and INGHRAM.[11] Single points from BREWER[7] and SEARCY[12] are also plotted and seem to agree with

[3] J. W. MELLOR *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Longmans, Green, London (1947).
[4] D. CUBICCIOTTI *J. Amer. chem. Soc.* **73**, 2032 (1951).
[5] J. B. CONWAY and M. S. KIRSHENBAUM *Ninth Progress Report*. High Temperature Project, Research Institute of Temple University. Contract N9-onr-87301. 1 January 1954.
[6] W. R. MOTT *Trans. Amer. electrochem. Soc.* **34**, 255 (1918).
[7] L. BREWER *Chem. Rev.* **52**, 55 (1953).
[8] *Selected Values of Chemical Thermodynamics Properties*. Natl. Bur. Stand. Circ. No. 500 (1952).
[9] M. HOCH, M. NAKATA and H. L. JOHNSTON *J. Amer. chem. Soc.* **76**, 2651 (1954).
[10] K. K. KELLEY *Bur. Mines. Bull.* 476 (1949).
[11] W. A. CHUPKA, J. BERKOWITZ and M. G. INGHRAM Argonne National Laboratory, Report to Office of Ordnance Research, U.S. Army (1955).
[12] A. SEARCY *Report UCRL-1404*. Univ. of California Radiation Laboratory (1951).

the high vapour pressure data. The extrapolation of these data to the melting point—2960°K—gives values of 10^{-2} and 7×10^{-5} atm, respectively. Further extrapolation to atmospheric pressure ($\log P = 0$) gives values of the boiling point of about 3700 and 4500°K, respectively (the extrapolation of solid vapour pressure data to the boiling point usually gives low values for the boiling point).

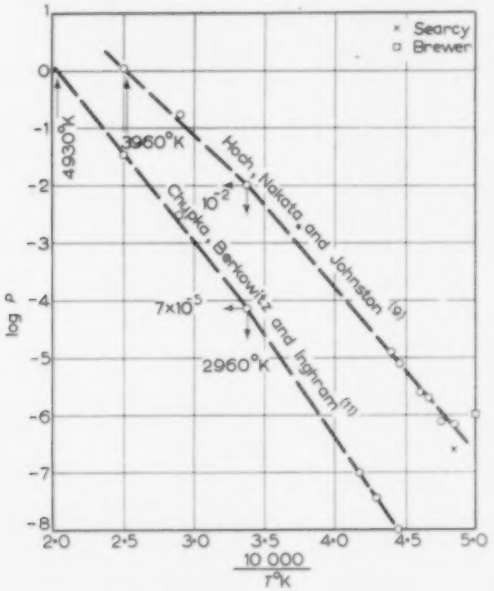

FIG. 1.—Vapour pressure of ZrO_2.

More representative values for the boiling point may be calculated by applying the Clausius–Clapeyron equation

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2} \tag{1}$$

to the liquid phase. Applying the Kirchhoff equation

$$\frac{d \Delta H_V}{dT} = (C_p)_V - (C_p)_L \tag{2}$$

and assuming $(C_p)_L = 20$ and $(C_p)_V = 10$ (see Table 2)

$$(\Delta H_V)_T = (\Delta H_V)_{2960} + \Delta C_p(T - 2960). \tag{3}$$

Substituting (3) in (1) and integrating

$$\ln P = \frac{-(\Delta H_V)_{2960}}{RT} + \frac{\Delta C_p}{R} \ln T + \frac{2960\ \Delta C_p}{RT} + C \tag{4}$$

where ΔH_V is the heat of vaporization and C is a constant of integration. This equation can now be used to calculate vapour pressures above the melting point.

The two sets of vapour pressure cited above give different values for the heat of

sublimation and hence different values are obtained for the heat of vaporization at the melting point. The data used in calculating the liquid phase vapour pressure values plotted in Fig. 1 are tabulated in Table 3. The boiling points are seen to be 4930 and 3960°K for the low and high vapour pressure data, respectively (an increase in ΔC_p of 5 caused by an error in $(C_p)_V$ or $(C_p)_L$, causes about a 100°K increase in

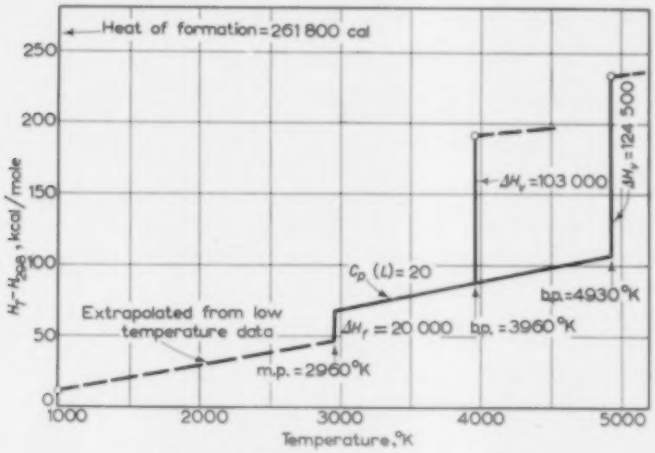

FIG. 2.—Enthalpy–temperature plot for ZrO_2.

the boiling points). The data of CHUPKA, BERKOWITZ and INGHRAM[11] therefore are in fairly good agreement with the boiling point reported by MOTT.[6]

It is believed that the data of INGHRAM[11] are substantially more reliable than the earlier results of HOCH *et al.*,[9] because the mass spectrometer method permits not only the determination of the concentration of a given species as a function of temperature, but also the identification of all species present in the vapour phase. A detailed critical review of the results of HOCH *et al.*[9] will be found in the INGHRAM paper.[11]

TABLE 3.—VALUES USED IN EVALUATING EQUATION (4)

	HOCH, NAKATA and JOHNSTON[9]	CHUPKA, BERKOWITZ and INGHRAM[11]
Heat of sublimation at 2960°K, cal/mole	134,100	165,000
Heat of vaporization at 2960°K, cal/mole	113,300	144,200
Vapour pressure of solid oxide at 2960°K	10^{-2}	7×10^{-5}
Constant of integration	59·9	60·3

An enthalpy–temperature plot for zirconium dioxide based on the thermodynamic data discussed above is shown in Fig. 2. From this plot it can be seen that the heat required to completely vaporize one mole of oxide is about 191,000 or 233,000 cal, depending upon which set of vapour pressure data is accepted. Since the heat available from the zirconium–oxygen reaction (261,800 cal/mole) is greater than

either of these, it would seem that the flame temperature would be much greater than 5000°K. This cannot be the case, however, inasmuch as the gaseous molecule will probably begin to dissociate at temperatures not much higher than the boiling point. It has been reported[7,9,11] that close to 2000°K, ZrO_2 vaporizes to a ZrO_2 molecule, and if this mechanism can be assumed to exist up to the boiling point the calculation of the flame temperature will be complete once the stability of ZrO_2 is established.

For the dissociation of $ZrO_2(g)$

$$ZrO_2(g) \rightarrow ZrO(g) + O(g) \tag{5}$$

the equilibrium constant can be calculated from published data using the equation:

$$\frac{\Delta F^\circ}{T} = \sum\left(\frac{F^\circ - H_0^0}{T}\right)_{\text{products}} - \sum\left(\frac{F^\circ - H_0^0}{T}\right)_{\text{reactants}} + \frac{\Delta H_0^0}{T} \tag{6}$$

Values for the free-energy function at 5000°K are given in Table 4. In estimating the value for $ZrO_2(g)$, the free-energy change for the following reaction was used:

$$Zr(g) + ZrO_2(g) \rightarrow 2ZrO(g) \tag{7}$$

At a temperature of 2408°K this value has been reported[11] as −33,000 cal. Since the free-energy function for $Zr(g)$ is known,[13] the only unknown is the free-energy

TABLES 4.—VALUES OF FREE ENERGY FUNCTION AT 5000°K

	$\left(\frac{F^\circ - H_0^0}{T}\right)$ cal/deg
$ZrO(g)$	−72·54[3]
$O(g)$	−47·64[3]
$Zr(g)$	−55·46[3]
$ZrO_2(g)$	−80·0 (estimated)

function for $ZrO_2(g)$, since ΔH_0^0 for the above reaction was reported as −14,400cal.[11] Substitution in an expression similar to (6) gives −74·6 as the free-energy function of $ZrO_2(g)$ at 2408°K. Extrapolation to 5000°K by comparing data presented by LATIMER[13] gives a value of −80·0. The value of ΔH_0^0 for the dissociation of $ZrO_2(g)$ can be obtained as follows:

$$Zr(g) + ZrO_2(g) \rightarrow 2ZrO(g) \qquad \Delta H_0^0 = -14{\cdot}400^{[11]}$$

$$ZrO(g) \rightarrow Zr(g) + O(g) \qquad \Delta H_0^0 = 180{\cdot}000^{[13]}$$

$$ZrO_2(g) \rightarrow ZrO(g) + O(g) \qquad \Delta H_0^0 = 165{\cdot}600$$

Substitution in equation (6) gives:

$$\Delta F^\circ_{5000^\circ K} = -35{,}300$$

This corresponds to almost complete dissociation (the gaseous ZrO molecule is about 25 per cent dissociated to atoms at 5000°K). In view of these data, the flame temperature will be limited to the boiling point (4930°K).

The above calculation can be repeated, using the less accurate data of HOCH, NAKATA and JOHNSTON[9] in which the ΔH_0^0 is 188,000 instead of 165,600 cal. Using

[13] W. M. LATIMER *Tables of Free Energy Functions.* MDDC-1462. Declassified 13 November 1947.

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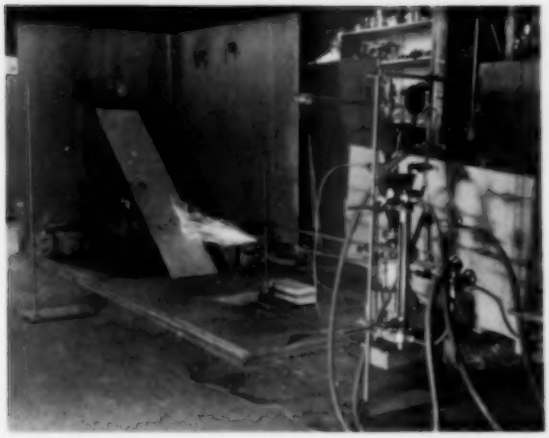

FIG. 3.—Powdered zirconium–oxygen flame, using large particle size.

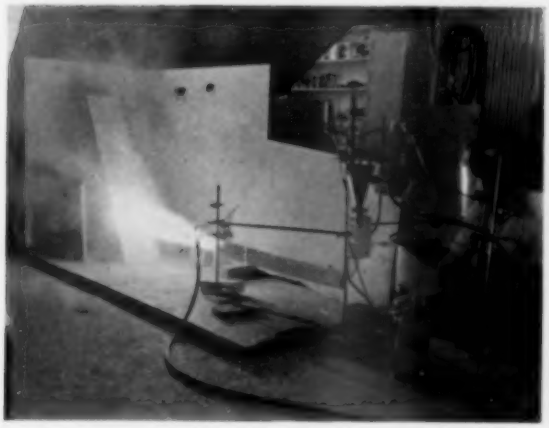

FIG. 4.—Powdered zirconium–oxygen flame in operation, using −200 mesh powder.

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this value, the dissociation of $ZrO_2(g)$ at the boiling point of 3960°K is only about 5 per cent and therefore sufficient heat is available to completely vaporize the oxide at the boiling point and to dissociate this small percentage of oxide. The flame temperature therefore will be slightly higher than the boiling point but will not be as high as 4500°K, since the dissociation of $ZrO_2(g)$ at this temperature is about 80 per cent.

EXPERIMENTAL

The operating techniques to be employed in producing powdered metal–oxygen flames have been described in detail.[1] Since oxygen is the conveying medium in torches of this type, satisfactory operation depends upon maintaining a linear velocity in the torch which is greater than the flashback velocity for the particular metal–oxygen dispersion. The extreme reactivity of zirconium powder dispersed in air or oxygen[2] would indicate that the flashback velocity for such mixtures should be quite large. Indeed, in the first attempts to operate such a torch, ignition (explosions) was obtained in the transport line leading to the torch and in some cases in the screw conveyor which fed the powdered metal into the oxygen stream. These ignitions were attributed to frictional heating of the particles in the screw conveyor and at the point of mixing where the oxygen stream picked up the metal particles delivered by the screw conveyor. It was clear, therefore, that special techniques were necessary in order to handle this extremely sensitive material.

The screw conveyor type of powder feed device was considered inadequate and was replaced by an over-pressure feed system. The powder storage tank (capacity of about 0·1 ft^3) used in this work had a removable venturi insert at the bottom, and a small argon over-pressure continuously maintained in this tank controlled the amount of powder delivered. An air-operated vibrator attached to the side of the storage tank kept the powder flowing freely.

In starting up, the valve at the bottom of the storage tank was closed and the argon pressure was adjusted to the desired powder rate. The pilot gas (hydrogen in this case), which flowed through a ring of holes surrounding the powder conduit at the face of the torch, was ignited and the oxygen rate adjusted to the proper value corresponding to the powder feed rate. The powder value was then opened and powdered zirconium was delivered to the flowing oxygen stream and then to the torch. The small amount of argon that flowed with the powder kept it in an inert atmosphere until it was picked up by the oxygen stream. This slight amount of argon did not affect the operating characteristics of the torch nor did it lower the flame temperature of the mixture significantly.

The zirconium powders used were all obtained from the Foote Mineral Co., Philadelphia, Pennsylvania. The characteristics of the powders tested are given in Table 5. The flame obtained using Type B (−80 + 100 mesh) is shown in Fig. 3 and is mostly a shower of sparks with poor combustion within the flame, due to the large particles. The flame obtained using Type C zirconium powder (248 g Zr/min and 90 l. O_2/min) is very similar to the one shown in Fig. 4. The flame was extremely bright (about 200,000 candle-power), and essentially complete combustion to ZrO_2 was obtained. The linear velocity through the torch tip was 275 ft/sec.

The flame shown in Fig. 4 has a temperature estimated to be about 4930°K (see Fig. 4). This is the highest metal flame temperature produced to date at a pressure

TABLE 5.—CHARACTERISTICS OF ZIRCONIUM POWDER TESTED

	A	B	C
Manufacturer's symbol	Type 120a	Type 2	Type 306-F-1*
Particle size	98–99%: −325 mesh	70-95%: −100 + 200 mesh: various screened fractions used	—
Total Zr	94% min	94% min	—
Flow characteristics	poor	good	good

* A sample of fines collected from the elutriation process in the manufacture of Type 2 powder.

of 1 atm. The highest non-metal flame temperatures reported in the literature are those of the C_4N_2–O_2 flame[14] at a temperature of 5260°K and the cyanogen–ozone flame[15] at 5200°K.

A detailed O.N.R. report on the oxy-zirconium flame has been published.[16]

Acknowledgements—The authors wish to express their thanks to the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1475, for their financial support of recent research in this field, and to the Office of Naval Research who sponsored our earlier work.

[14] A. D. KIRSHENBAUM and A. V. GROSSE *J. Amer. chem. Soc.* **78**, 2020 (1956).
[15] A. G. STRENG and A. V. GROSSE *J. Amer. chem. Soc.* **79**, 1517 (1957).
[16] J. S. CONWAY and A. V. GROSSE *Final Report* pp. 2–30. High Temperature Project, Research Institute of Temple University, Contract N9-onr-87301. 1 July 1954.

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EQUILIBRIUM STUDIES ON NATURAL ION-EXCHANGE MINERALS—II

CAESIUM, SODIUM AND AMMONIUM IONS

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Abstract—Isotherms and values of thermodynamic equilibrium constants have been derived for exchange within the systems Cs^+–Na^+ and Cs^+–NH_4^+ upon lower greensand soil; solid phase activity coefficients have also been calculated. The results are compared with those of other workers on pure clay minerals; as in the case of the Cs^+–Sr^{2+} exchange, it is found that the equilibrium is less favourable towards Cs than for pure montmorillonite, but more so than for attapulgite, confirming the intermediate position of the mixed-clay mineral in the case of the soil.

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THE possible use of soils for decontamination of low-activity wastes has been discussed in Part I,[1] which also records the results of ion-exchange studies on a particular soil with caesium and strontium ions. In order to make the most efficient use of such an ion-exchange system, it would be preferable to first remove the bulk of the bivalent and trivalent ions from solution, in order that they should not compete with monovalent ions such as caesium which it is required to remove on the ion-exchange bed. After standard precipitation and settling treatment as used in commercial water-treatment installations, the waste solution entering the soil bed will contain caesium, sodium, and ruthenium, together with much smaller amounts of other ions. It is therefore necessary to examine the behaviour of the soil towards the mixed system ($Cs^+ + Na^+$), both as regards the ion-exchange equilibrium and the flow properties of the system, since deflocculation of the clay fraction usually results on treating soils with sodium ion, with considerable swelling and decrease in flow-rate.

Results reported for the system Cs^+–Na^+–attapulgite[2] show that the equilibrium constant for the exchange

$$Na^+ + \text{Cs-clay} \rightleftharpoons Cs^+ + \text{Na-clay}$$

is 0·041 at 30°C; in view of the similarity between the two systems it was expected that a similar value of K would be obtained for the lower greensand soil, and that Cs would be predominantly exchanged on the column. Although no values are given in the literature for the equilibrium constant of the Cs–Na exchange on montmorillonite, corrected data for the elution of Cs^+ from montmorillonite by Na^+[3] enable part of the isotherm to be drawn, and show that equilibrium favours Cs even more strongly than in the case of attapulgite.

Although data exist for all the alkali metals except Rb in the case of attapulgite,[2]

[1] C. B. AMPHLETT and L. A. MCDONALD *J. inorg. nucl. Chem.* **2**, 403 (1956).
[2] C. N. MERRIAM and H. C. THOMAS *J. chem. Phys.* **24**, 993 (1956).
[3] J. A. FAUCHER, R. W. SOUTHWORTH and H. C. THOMAS *J. chem. Phys.* **20**, 157 (1952).

and for Cs, Na, and K in the case of montmorillonite,[3,4] there are no thermodynamic results reported for the ion NH_4^+, which on grounds of size and exchange potential would be expected to be close to K^+ in the series. Considerable use is made of NH_4^+ solutions in soil chemical studies, and for these reasons it was included in the present investigation.

EXPERIMENTAL

The treatment of the soil and details of the column experiments are described in Part I.[1] ^{137}Cs was used as tracer, solutions consisting of traced ($CsNO_3$ + NH_4Cl) or ($CsNO_3$ + NaCl). Equilibrium techniques were used throughout, with solutions ranging from 0·02 to 0·10 N total ionic concentration. Owing to the very strong absorption of Cs^+ relative to Na^+, the more concentrated solutions were used when low ratios of Cs : Na were involved; otherwise, an excessively long time was needed to attain equilibrium conditions.

RESULTS

From the breakthrough curves obtained by the equilibrium technique values were obtained of the relative Cs content of the solid phase q_{Cs}/q_0 in equilibrium with a solution in which the relative Cs concentration was c_{Cs}/c_0; q and c are expressed in milliequivalents (mequiv./g and mequiv./ml respectively. Tables 1 and 2 give the values of q/q_0 and of c/c_0 for the two systems, while Figs. 1 and 2 show the isotherms obtained by plotting q/q_0 vs. c/c_0.

DISCUSSION

The exchange equilibrium for two monovalent ions may be written

$$CsX + M^+ \rightleftharpoons Cs^+ + MX$$

where X represents the exchange matrix (in this case the clay components of the soil) and M^+ is either Na^+ or NH_4^+ ion. If c_0 is the total ionic concentration of the solution, c that of Cs^+ ion, q_0 the exchange capacity of the soil and q the capacity for Cs in the presence of the other cation, then the concentration ratio may be written as

$$K'_c = \frac{\text{concentration of } Cs^+ \text{ in solution} \times \text{concentration of } M^+ \text{ in solid}}{\text{concentration of } Cs^+ \text{ in solid} \times \text{concentration of } M^+ \text{ in solution}}$$

$$= \frac{c(q_0 - q)}{q(c_0 - c)} = \frac{(c/c_0)(1 - q/q_0)}{q/q_0(1 - c/c_0)} \qquad (1)$$

It will be seen that, unlike the Cs–Sr system, K'_c is independent of the total concentration c_0 (Figs. 1 and 2). The thermodynamic equilibrium constant is given by the expression

$$K = K'_c \gamma_{Cs} f_M / \gamma_M f_{Cs} = K_c f_M / f_{Cs} \qquad (2)$$

where the γ's are activity coefficients in solution and the f's those in the solid phase.

From the theory developed by GAINES and THOMAS,[5] K is given by the following expression for an exchange between monovalent ions.

$$\ln K = \ln f_M(A)/f_{Cs}(B) + \int_0^1 \ln K_c \, . \, d(q/q_0) - \int_A^B N_s \, . \, d \ln a_s \qquad (3)$$

The symbols have the same meaning as in Part I. If we make the same assumptions as in Part I, viz. that the pure mono-ion clays are taken as standard states and that

[4] J. A. FAUCHER and H. C. THOMAS *J. chem Phys.* **22**, 258 (1954).
[5] G. L. GAINES and H. C. THOMAS *J. chem Phys.* **21**, 714 (1953).

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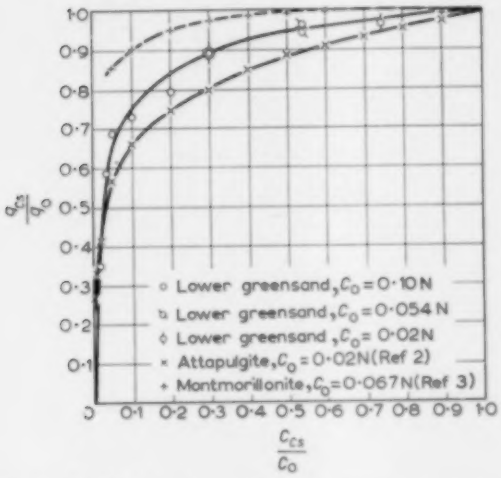

FIG. 1.—Cs^+–Na^+ isotherm on lower greensand at room temperature.

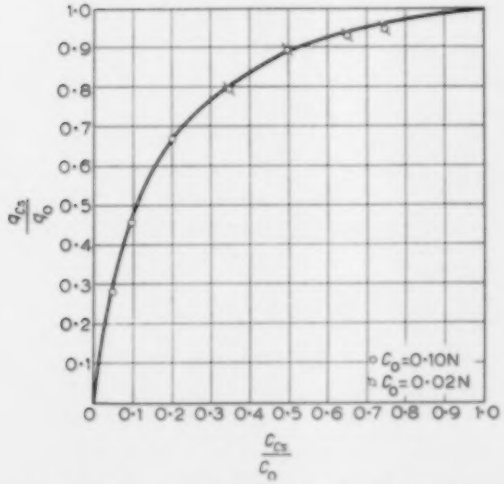

FIG. 2.—Cs^+–NH_4^+ isotherm on lower greensand at room temperature.

the change in water activity a_s is negligible, then the first and third terms vanish. Moreover, in dilute solutions of mixed monovalent ions the ratio γ_{Cs}/γ_M will be approximately unity, so that K_c may be replaced by the experimentally determined quantity K'_c, and equation (3) becomes

$$\ln K \simeq \int_0^1 \ln K'_c \, . \, d(q/q_0) \tag{4}$$

The last assumption is much more reliable in this case than in the case of the Cs^+–Sr^{2+} exchange, where $\gamma_{Cs}^2/\gamma_{Sr}$ deviates appreciably from unity; as shown below, it is possible to correct the earlier values for the Cs^+–Sr^{2+} system[1] in order to eliminate

this error. Values of K'_c for the systems Cs^+–Na^+ and Cs^+–NH_4^+ are given in Tables 1 and 2, while Fig. 3 shows the dependence of $-\ln K'_c$ upon q/q_0; K was determined by integration under the curves in Fig. 3. Owing to the steepness of the isotherms in the region of $c/c_0 = 0$, 1, it is difficult to obtain reliable values of K'_c near the

TABLE 1.—UPTAKE OF Cs^+ IN THE PRESENCE OF Na^+ ION

(a) Experimental

C_0, mequiv./ml	C/C_0	q/q_0	$10^2\ K'_c$	$-\ln K'_c$
0·0999	0·020	$0·35_1$	3·78	3·26
0·1001	0·035	$0·58_4$	2·58	3·66
0·1001	0·050	$0·68_6$	2·39	3·74
0·1001	0·101	$0·72_9$	4·17	3·18
0·1000	0·201	$0·79_6$	6·45	2·74
0·1001	0·301	$0·89_2$	5·22	2·95
0·0202	0·303	$0·88_6$	5·59	2·88
0·0544	0·542	$0·94_9$	6·36	2·76
0·0544*	0·542	$0·95_6$	5·45	2·91
0·0201	0·746	$0·96_4$	10·96	2·16

(b) From smoothed isotherm

0·01	0·170	4·93	3·01
0·02	0·340	3·96	3·23
0·03	0·510	2·97	3·52
0·04	0·648	2·26	3·79
0·05	0·682	2·46	3·71
0·1	0·737	4·12	3·19
0·2	0·825	5·31	2·94
0·4	0·918	5·96	2·82
0·6	0·957	6·74	2·70

* Uptake on soil with 80 per cent Na, 20 per cent Cs instead of natural Ca soil.

end of the curve, either experimentally or by interpolation. FAUCHER and THOMAS[6] have shown that the isotherm is linear in this region, and that the values of K'_c at the two ends of the curve are related to the limiting slope of the curve. In the case of a 1 : 1-exchange, the limiting values are given by the expression

$$\lim_{c \to 0,1} (\ln K'_c) = -\ln S \qquad (5)$$

where S is the slope. This relationship has been used to derive the intercepts in Fig. 3, although it is obvious that the uncertainty in these points is quite large.

As in the case of montmorillonite[3] and attapulgite,[2] exchange favours Cs relative to Na, the isotherm for lower greensand lying between the others. Equilibrium data for montmorillonite have not been obtained, and the curve given in Fig. 2 was derived by correcting elution data for the non-equilibrium conditions during elution;[3] consequently, the isotherm is incomplete and K cannot be derived. The value of K for greensand at 20°C is 0·057, which is close to that for attapulgite, viz. 0·033 extrapolated to 20°C from data given by MERRIAM[2] for 0·02 N solutions

[6] J. A. FAUCHER Thesis, Yale University (1953).

TABLE 2.—UPTAKE OF Cs^+ IN THE PRESENCE OF NH_4^+ ION

(a) Experimental

C_0, mequiv./ml	C/C_0	q/q_0	$10^2 K'_c$	$-\ln K'_c$
0·1000	0·050	0·282	0·134	2·01
0·1000	0·100	0·454	0·134	2·01
0·1001	0·200	0·670	0·123	2·10
0·0200	0·350	0·796	0·138	1·98
0·0201	0·500	0·895	0·117	2·19
0·0200	0·651	0·933	0·134	2·01
0·0200	0·751	0·945	0·176	1·74

(b) From smoothed isotherm

	0·01	0·074	0·126	2·072
	0·02	0·139	0·126	2·072
	0·03	0·197	0·126	2·072
	0·04	0·241	0·131	2·033
	0·05	0·282	0·134	2·010
	0·1	0·446	0·138	1·981
	0·2	0·663	0·127	2·064
	0·3	0·765	0·132	2·025
	0·4	0·832	0·135	2·003
	0·5	0·883	0·133	2·018
	0·6	0·917	0·137	1·988
	0·7	0·942	0·144	1·938
	0·8	0·962	0·158	1·845
	0·9	0·980	0·184	1·693

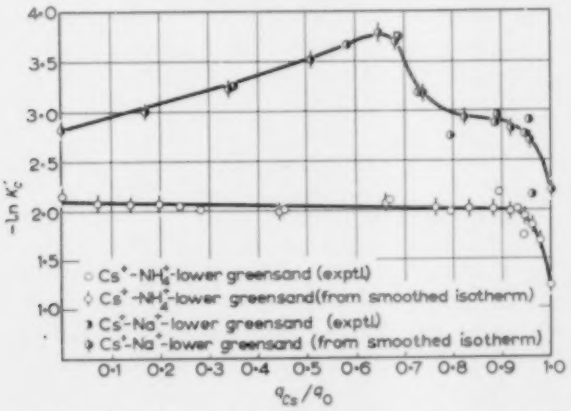

FIG. 3.—Variation of ln K'_c with q/q_0 for the systems Cs^+–Na^+ and Cs^+–NH_4^+.

at 75 and 30°C. The Cs^+–NH_4^+ system also favours Cs, although much less so than in the Cs^+–Na^+ case, the value of K being 0·128 at approximately 20°C; this is close to the extrapolated value of 0·116 for the Cs^+–K^+ exchange on attapulgite;[2] in view of the similarity between the values of $K(Na^+ \rightarrow Cs^+)$ for greensand and for attapulgite, and the similarity in hydrated ionic radii of K^+ and NH_4^+ ions (K^+ and NH_4^+ are usually found adjacent to each other in the Hofmeister series),

this probably indicates similar values for $K(NH_4^+ \rightarrow Cs^+)$ for the two exchangers. $K(K^+ \rightarrow Cs^+)$ for montmorillonite is appreciably smaller than for attapulgite, viz. 0·076,[4] so that once again we would expect the isotherm for greensand to lie between those for the two clays. As in the case of the Cs–Sr system,[1] the differences between the soil and montmorillonite may be explained on the basis of the presence of illite in the clay fraction of the former; this clay mineral appears to exhibit a smaller preference for Cs than does montmorillonite. A decreased affinity for Cs relative to the other alkali metal cations is also shown by the micaceous clay mineral

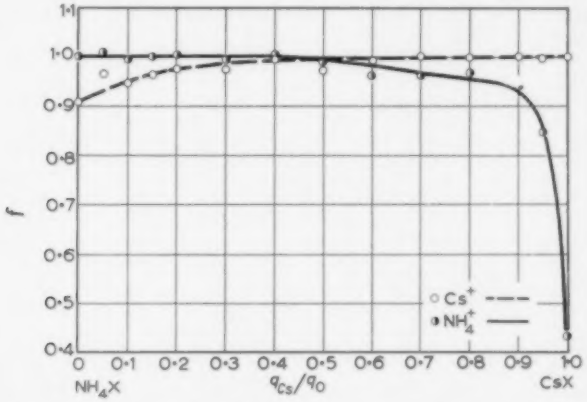

FIG. 4.—Solid phase activity coefficients in the system Cs^+–NH_4^+–lower greensand.

muscovite,[7] which resembles illite structurally. The position of the greensand isotherms relative to the montmorillonite isotherms is thus explained qualitatively.

The solid-phase activity coefficients for a 1 : 1 exchange, making the same simplifying assumptions as in Part I, are given by the expressions below.

$$\ln f_{Cs}(Q) = (1 - q/q_0) \ln K'_c(Q) - \int_{q/q_0}^{1} \ln K'_c \, . \, d(q/q_0) \qquad (6)$$

$$\ln f_M(Q) = -(q/q_0) \ln K'_c(Q) + \int_{0}^{q/q_0} \ln K'_c \, . \, d(q/q_0) \qquad (7)$$

where the standard states of unit activity are taken as the pure mono-ion exchangers in contact with a solution containing only the one ion; Q refers to the value of q/q_0 upon the curve at which the activities are calculated. Values of f_{Cs} and f_{NH_4} calculated by this method are shown in Fig. 4. The behaviour of the two ions Cs^+ and NH_4^+ is much more nearly ideal than that of Cs^+ and Na^+ or of Cs^+ and Sr^{2+} (Part I) in soils containing both ions; this is reflected also in the relative constancy of K'_c for the first case up to a value of $q/q_0 \simeq 0{\cdot}95$ (Fig. 3), and is probably due to the much greater similarity in ionic radii. On the other hand, both Cs^+ and K^+ show much greater deviation from ideality in attapulgite, though not as much as do Cs^+ and Na^+. While the activity coefficient plots for the Cs–NH_4 system were satisfactory, those for the Cs–Na system show unexplained wide deviations over the range of q/q_0 from 0·3 to 0·75, despite the generally good behaviour of the isotherm

[7] P. SCHACHTSCHABEL. *Kolloidbeihefte* **51**, 199 (1940).

and of the individual uptake curves. This range of q/q_0 corresponds to values of c/c_0 from 0·015 to 0·1, i.e. at the extreme end of the isotherm at high relative Na concentrations, where the uncertainty in measurement is great, and where effects of the relatively high Na concentrations upon the soil itself may be appreciable, particularly since in this region solutions of higher total ionic concentration are employed.

TABLE 3.—SUMMARIZED DATA FOR EXCHANGE ON LOWER GREENSAND AND ON CLAYS

System	K	$\Delta G^\circ = -RT \ln K$	Reference
	Lower greensand (20°C)	cal/mole	
$Sr^{2+} \rightarrow Cs^+$	$6{\cdot}27 \times 10^{-4}$ ($c_0 = 0{\cdot}02$N)	3900	(1)
	$6{\cdot}48 \times 10^{-4}$ ($c_0 = 0{\cdot}05$N)	3870	
$Na^+ \rightarrow Cs^+$	0·057	1850	This
$NH_4^+ \rightarrow Cs^+$	0·128	1190	paper
	Montmorillonite		
$Sr^{2+} \rightarrow Cs^+$	$1{\cdot}9 \times 10^{-4}$ (25°C)	3700	(8)
$K^+ \rightarrow Cs^+$	0·076 (20°C)	1500	(4)
	Attapulgite		
$Li^+ \rightarrow Cs^+$	0·029	2140	
$Na^+ \rightarrow Cs^+$	0·041	1930	(2)
$K^+ \rightarrow Cs^+$	0·131	1220	
$Na^+ \rightarrow K^+$	0·109	1340	

The uncertainty at this end of the isotherm will also lead to an uncertainty in the intercept for ln K'_c for the Cs–Na system at $c = 0$, which will affect all subsequent calculations. Consequently, the values of f_{Cs} and f_{Na} in this system will be extremely rough ones, and the value of K will be less certain than those for the other systems studied. There is also some uncertainty (due to experimental variations) about the exact position of the central portion of the Cs–Na isotherm in Fig. 1, but the effect of this upon values of K and of the activity coefficients is found to be slight.

Table 3 gives the values of K and of ΔG^0 ($= RT \ln K$) for the exchange reactions studied on lower greensand and on various clays. The values of K for the Cs–Sr exchange in this table have been corrected from those given in reference (1) for activity coefficient ratios in solution. Since the expression for ln K involves ln K_c, and since $K_c = K'_c \gamma_{Cs}^2/\gamma_{Sr}$, the correction to the value of ln K involves the addition of the term $\int_0^1 (\gamma_{Cs}^2/\gamma_{Sr}) d(q/q_0)$. To a first approximation (and within the accuracy of these results) we may neglect interaction terms in deriving the activity coefficients for mixed electrolyte solutions, and insert values of the coefficients for single salt solutions in the ratio

$$\gamma^2_{Cs}/\gamma_{Sr} = \gamma_{\pm}{}^4 CsNO_3/\gamma_{\pm}{}^3 Sr(NO_3)_2,$$

whence $$\log (\gamma_{Cs}{}^2/\gamma_{Sr}) = 4 \log \gamma_{\pm CsNO_3} - 3 \log \gamma_{\pm Sr(NO_3)_2}$$

Values of $\gamma_{\pm}$ were calculated using the Debye–Huckel expression

$$\log \gamma_{\pm} = -\frac{z_1 z_2 . A\sqrt{I}}{1 + Ba\sqrt{I}}$$

where $A = 0{\cdot}5028$ and $B = 0{\cdot}3273$ at 18°C;[8] values of $\mathring{a}$ were taken as 3·0 Å for $CsNO_3$ and 4·6 Å for $Sr(NO_3)_2$.[9] $I = c_{Cs} + 1{\cdot}5\, c_{Sr}$, where c is the concentration in equivalents/l. In this way values of $\gamma_{Cs}{}^2/\gamma_{Sr}$ were calculated for $c/c_0 = 0 - 1$ and for $c_0 = 0{\cdot}02$ and 0·05 N. It was found that $\gamma_{Cs}{}^2/\gamma_{Sr}$ varied only slightly, from 0·137 to 0·151 at 0·05 N and from 0·099 to 0·117 at 0·02 N, and therefore mean values were taken instead of integrating. The reliability of this approximate treatment may be judged by comparing the value of 0·331 for $\ln \gamma_{Cs}{}^2/\gamma_{Sr}$ at 0·05 N with that of 0·406 obtained by more rigorous treatment,[7] using GLUECKAUF's equation,[10] for the activity coefficients in mixed electrolyte solutions. Within the accuracy of these experiments the approximate treatment is sufficient, since such a variation in $\ln (\gamma_{Cs}{}^2/\gamma_{Sr})$ produces only a 1 per cent variation in $\ln K$.

[8] G. L. GAINES and H. C. THOMAS *J. chem. Phys.* **23**, 2322 (1955).
[9] R. A. ROBINSON and R. H. STOKES *Electrolyte Solutions* App. 8.10. Butterworths, London (1955).
[10] R. H. STOKES and R. A. ROBINSON *J. Amer. chem. Soc.* **70**, 1870 (1948).
[11] E. GLUECKAUF *Nature, Lond.* **163**, 414 (1949).

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ION-EXCHANGE STUDIES OF SOLUTIONS OF TELLURATES

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Abstract—The sorption of tellurium and of chloride by Amberlite I.R.A. 400–Cl from telluric acid solutions, containing 1·0–0·07 g atoms of tellurium per litre, has been studied at various pH values. The results have been interpreted in terms of the sorption of a tetra- and a tri-tellurate ion, in addition to the non-condensed ions $H_5TeO_6^-$ and $H_4TeO_6^{--}$. The actual ions sorbed appear to depend both upon the pH and the tellurium concentration of the solutions. An attempt was made to correlate the data obtained by ion-exchange methods with those supplied by an examination of the ultra-violet absorption spectra of telluric acid and sodium tellurate solutions.

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THE fact that orthotelluric acid and its alkali salts have a tendency to polymerize in solution appears to have been first reported by ROSENHEIM and JANDER[1] as a result of conductivity measurements. They stated that the formation of polymers, which are more strongly ionized than simple orthotelluric acid, is favoured by increasing the telluric acid concentration or by heating the solution. In the latter case a colloidal solution is eventually obtained, which nevertheless reverts partially or wholly to its original state on cooling. At low temperatures cryoscopic measurements indicated that only a very small proportion of the acid exists in the polymeric form.

Subsequently GHOSH and DHAR[2] studied the coagulation of telluric acid sols by alkali metal chlorides in the presence of various quantities of hydroxyl ion. Their results indicated that the polyacid may be broken down to simple telluric acid by raising the pH value of the solution.

The constitution of allo-telluric acid $(H_2TeO_4)_n$, formed by heating the solid ortho-acid in a sealed tube at 140°, has been extensively investigated by PATRY.[3] His conductivity and neutralization experiments suggest that the allo-acid is tenfold polymerized, whereas ebullioscopic data on the methyl and ethyl esters gives the degree of polymerization as 11 ± 1. The conductivity of the allo-acid was found to be three or four times greater than that of orthotelluric acid, but this value gradually falls on standing, indicating a depolymerization which takes about three days for completion (see also ref. 4).

SOUCHAY and TEYSSEDRE[5] have studied orthotelluric acid and sodium tellurate solutions (0·125–1·5 g atoms of tellurium per litre) by cryoscopy, titration experiments, pH measurements and by partition work using butyl alcohol and water. This work

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[1] A. ROSENHEIM and G. JANDER *Kolloidzschr.* **22,** 23 (1918); *J. chem. Soc.* **114,** 194 (1918).
[2] S. GHOSH and N. R. DHAR *Z. anorg. Chem.* **190,** 421 (1930).
[3] M. PATRY *Bull. Soc. chim. Fr.* **3,** 845 (1936); P. PASCAL and M. PATRY *C. R. Acad. Sci., Paris* **200,** 710 (1935).
[4] J. W. MELLOR *Inorganic and Theoretical Chemistry* Vol. XI, p. 83 *et seq.* Longmans, Green, London (1931).
[5] P. SOUCHAY and M. TEYSSEDRE *C. R. Acad. Sci., Paris* **236,** 1965 (1953).

was later extended and reported more fully by LOURIJSEN-TEYSSEDRE.[6] It appears that both di- and tetra-condensed tellurate ions may be present at some stage in a solution of a tellurate and that the state of condensation of telluric acid depends on two factors, the concentration and the pH of the solution.

Conductometric studies of solutions of orthotelluric acid have been carried out by EARLEY and EDWARDS,[7] who conclude that a dimer and a trimer are found in solutions containing up to 1·0 g atoms of tellurium per litre, but they suspect that polyacids of a yet higher degree of condensation may be present in more concentrated solutions. This is in agreement with later conductivity studies due to ANTIKAINEN.[8]

The ultra-violet absorption spectra of telluric acid solutions were originally studied by STUBER, BRAIDA and JANDER,[9] who found that a considerable displacement of the absorption edges was brought about by a change in the pH of the solution. This was thought to be analogous to the visible colour change observed in solutions of dichromates as a decondensation to the chromate is brought about by increasing the pH of the solution. But as STUBER *et al.* could not detect the presence of polytelluric acids by cryoscopy or diffusion studies, they suggested a mechanism which did not involve the presence of condensed ions in order to explain the behaviour of the ultra-violet spectrograms.

The present ion-exchange study of telluric solutions has been prompted by the success of this method in the investigation of solutions of three other weak acids: germanic,[10] boric,[11] and arsenious,[12] which all yield condensed ions. Preliminary studies have shown that telluric acid is sorbed on the strongly basic anion-exchanger Amberlite I.R.A. 400 in the chloride form.

It was also decided to attempt a qualitative correlation between the results of ion-exchange and spectrophotometry to find if the ionic system present in the tellurate solutions is in any way altered by the introduction of the resin.

EXPERIMENTAL

Solutions. Stock solutions (containing 1·5, 0·75, 0·62, 0·42, 0·30, 0·21 and 0·10 g atoms of tellurium per litre) were prepared by dissolving analytical grade telluric acid in boiled-out distilled water. Portions of these solutions (50 ml) were adjusted to the required pH by addition of sodium hydroxide, and were then made up to 75 ml by addition of water before introducing the resin. In this way, test solutions containing 1·0, 0·5, 0·41, 0·28, 0·20, 0·14 and 0·07 g atoms of tellurium per litre were obtained.

Anion-exchanger. Amberlite I.R.A. 400-Cl (1·0 g) was used; it was prepared from the hydroxide form by treatment with 2 N HCl, washing free from excess acid and air-drying before use. All washing water used in these experiments was previously deionized by passing through a column of Permutit "Bio-Deminrolit" mixed bed resin.

Equilibrium experiments. At least two days were allowed for equilibrium to be established between resin and solution phases, each resin-solution mixture being mechanically shaken for about two hours daily. The solution and resin phases were then separated by filtration through a dry column (approx. 10 cm long, 1 cm i.d.) containing a glass-wool plug, the filtrate being retained for analysis. The resin was then completely transferred to the column by a jet of water, and was then washed by slow passage of a further 200 ml of water. The chloride still on the resin was then eluted with 300 ml of 2 N HNO_3 and analysed in the eluate. The resin was then reconverted to

[6] M. LOURIJSEN-TEYSSEDRE *Bull. Soc. Chim. Fr.* **22,** 1196 (1955).
[7] H. EARLEY and J. O. EDWARDS *Office of Ordinance Research Project, No.* 1349.
[8] P. ANTIKAINEN *Acta chem. fenn.* B **30,** 22 (1957).
[9] C. STUBER, A. BRAIDA and G. JANDER *Z. phys. Chem.* A **171,** 320 (1934).
[10] D. A. EVEREST and J. E. SALMON *J. chem. Soc.* 2438 (1954).
[11] D. A. EVEREST and W. J. POPIEL *J. chem. Soc.* 3183 (1956).
[12] D. A. EVEREST and W. J. POPIEL *J. chem. Soc.* 2433 (1957).

the chloride form by passing 300 ml of 2 N HCl and then washing free from excess acid. The capacity of the resin sample for chloride ions was then determined by eluting with 2 N HNO_3 and analysing the eluate as before.

Analytical methods. Tellurium in the filtrate was determined by first neutralizing aliquot portions with dilute nitric acid (methyl orange) and then titrating with sodium hydroxide after addition of mannitol.[12]

Chloride was determined gravimetrically as silver chloride. The quantity "chloride desorbed" from the resin was found from the difference between the total capacity and the chloride loading at equilibrium for a given resin sample.

Measurements of pH were made with a commercial-type pH metre, glass electrode and saturated calomel electrode. For strongly alkaline solutions, a Cambridge Instrument Co. "Alki" glass electrode was used.

Ultra-violet absorption spectra. Measurements on telluric acid solutions were carried out with a Unicam SP-500 single-beam spectrophotometer. Reference solutions contained the same quantity of sodium hydroxide as the test solutions.

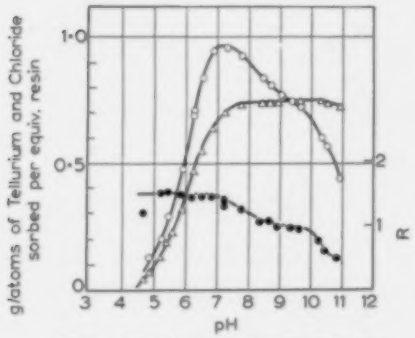

FIG. 1.—Sorption of tellurium and chloride by Amberlite I.R.A. 400–Cl (1·0 g). Concentration of Te in solution = 0·14 g atom Te/l.
○ Sorption of tellurium
△ Desorption of chloride
● *R* values

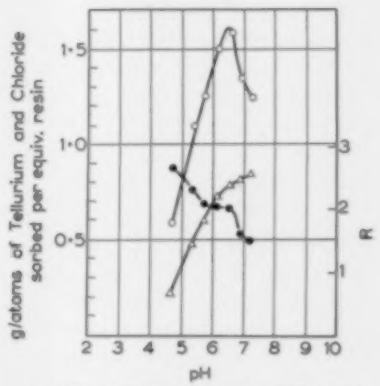

FIG. 2.—Sorption of tellurium and chloride by Amberlite I.R.A. 400–Cl (1·0 g). Concentration of Te in solution = 0·5 g atom Te/l.
○ Sorption of tellurium
△ Desorption of chloride
● *R* value

RESULTS

For each telluric acid concentration studied the quantity of tellurium sorbed by the resin, the chloride desorbed and the ratio of g atoms of tellurium sorbed to g atoms of chloride desorbed (referred to in the discussion as the *R* value) were plotted against the equilibrium pH value. The *R* value, which is in effect the average number of tellurium atoms sorbed per active site of the resin, is used to determine the number of tellurium atoms present in the actual tellurate ions sorbed.[11,12,13] Experiments were carried out with the tellurium solutions previously listed and the results for solutions containing 0·14 and 0·5 g atoms of tellurium are given in Figs. 1 and 2. The results obtained with these solutions were typical of those found at the other concentrations studied; more detailed results are given elsewhere.[14]

It was found that solutions of telluric acid containing 1·0–0·28 g atoms of tellurium all showed a pH region where the *R* value remained steadily at 2. In the less concentrated solutions, containing 0·2–0·07 g atoms of tellurium, the maximum *R* value

[12] F. FOUASSON *Ann. Chim.* **3**, 594 (1948).
[14] W. J. POPIEL Ph. D. Thesis, London (1957).

obtained was 1·5. Also, as seen from Fig. 1, a point of inflexion is obtained in the R value curve at $R = 1$.

For each of the concentrations studied, the sorption of tellurium reaches a maximum at a pH value depending on the tellurium concentration of the solution, such that the lower the concentration the higher was the pH value corresponding to the maximum sorption of tellurium.

The ultra-violet spectrograms obtained with telluric acid solutions containing

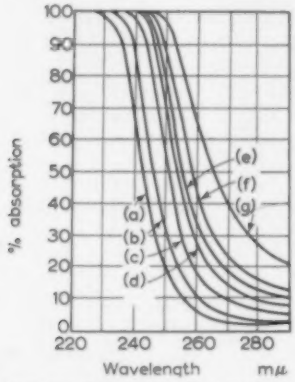

FIG. 3.—Absorption spectrograms (1 cm cells) of solutions containing (a) 0·05: (b) 0·1: (c) 0·2: (d) 0·3: (e) 0·4: (f) 0·5 and (g) 0·6 g atoms of tellurium per litre.

0·14 g atoms of tellurium show sharp absorption edges which move to longer wavelengths as the pH of the solution is increased. This bears resemblence to the spectrograms obtained for arsenious acid[12] and is in agreement with the observations of other workers.[9,15] On increasing the concentration of the telluric acid solutions, the absorption spectrograms likewise move to longer wavelengths (Fig. 3), but this displacement is not so marked as that brought about by increasing the pH.

DISCUSSION

From crystallographic evidence, solid orthotelluric acid is made up of octahedral $Te(OH)_6$ units joined by hydrogen bonds.[16] On the assumption that the structure of telluric acid in the solid state and in a concentrated aqueous solution differs only in degree and not in kind, we would expect a decondensation to be observed on diluting a solution of the acid, resulting from a gradual breakdown of the hydrogen bonds between the telluric acid molecules and their replacement by bonds between the acid and water.

The influence of the hydroxyl ion on the condensation state of the tellurate ion may be shown as follows:

$$n\mathrm{TeO_4^{=}} + 2m\mathrm{H^+} \rightleftarrows [\mathrm{Te}_n\mathrm{O}_{4n-m}]^{(2n-2m)-} + m\mathrm{H_2O}$$

this being similar to the mechanism put forward for the condensation of the molybdate ion.[17] For the sake of simplicity the formula for telluric acid used is the one

[15] L. W. SCOTT and G. W. LEONARD *Analyt. Chem.* **26**, 445 (1954).
[16] L. PASSERINI and M. A. ROLLIER *Atti accad. Lincei* **21**, 364 (1935); L. PAULING *Z. Kristollogr.* **91**, 367 (1935).
[17] H. J. EMELEUS and J. S. ANDERSON *Modern Aspects of Inorganic Chemistry* p. 212. Routledge and Kegan Paul, London (1952).

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analogous to sulphuric acid, although it is now accepted that it should include two molecules of water of constitution. It may be seen that the presence of the hydroxyl ion will displace the equilibrium to the left in favour of the non-condensed tellurate species.

In the light of the above considerations, the results of the present work may be explained by assuming a decondensation to take place either on dilution or on raising the pH of the solution, with the successive presence of the tetra-, tri-, and possibly also the di-tellurate ions. Alkali salts derived from the hypothetical polytelluric acids $H_2Te_4O_{13}$, $H_2Te_3O_{10}$, and $H_2Te_2O_7$ have been known for some time.[18] We shall use these formulae for convenience, although they may not necessarily represent the true state of the polytellurate ions in solution and overmuch significance should not be attached to them.

Thus the R values greater than 2, which occur with solutions containing more than 0·5 g atoms of tellurium per litre (see Fig. 2), may be explained by the sorption on the resin of a mixture of $HTe_4O_{13}^-$ ($R = 4$) and $Te_4O_{13}^{=}$ ($R = 2$). The divalent tetratellurate ion appears to be especially stable over a relatively wide pH and concentration range, as shown by a steady R value of 2 occurring at low pH values in solutions containing 1·0–0·28 g atoms of tellurium per litre. A further decondensation to $Te_3O_{10}^-$ will explain the steady maximum R value of 1·5 obtained with solutions containing 0·2–0·07 g atoms of tellurium per litre. Although it would be logical to expect that the $HTe_3O_{10}^-$ ion occurs as an intermediate, the sorption of this ion is not indicated by the present method and it is possible that it does not occur in sufficient quantity in solution to be detected.

In solutions containing 0·14 g atoms of tellurium per litre or less the decondensation of the polytellurate ions to simple $H_5TeO_6^-$ appears to be complete at pH 9, as shown by an R value of unity in the pH region 9–10. As the pH is further increased, the value of R decreases until it approaches 0·5($H_4TeO_6^{=}$) at about pH 11. It is noteworthy that although solutions containing 0·14 g atoms of tellurium per litre were found to be stable up to about pH 7, an even microcrystalline precipitate occurred on the walls of the flask after 2 days if the solution was in the pH range 7–9·5, crystallization being most ready at pH 8–9. It was found that the Na/Te ratio in solution then approached unity, and the salt that crystallized was found to have a Na/Te ratio corresponding to NaH_5TeO_6. In the pH region 9·5–11·5, no crystallization took place and the solutions appeared stable indefinitely, but at higher pH values the solutions deposited clumps of crystals after about 2 days which were visibly different to those obtained at pH 8–9. On analysis these proved to have an Na/Te ratio corresponding to $Na_2H_4TeO_6$. These observations are in agreement with the work of FOUSSON,[13] who has extensively investigated the conditions for formation of mono- and di-sodium tellurates.

We, may account, therefore, for the observed trend in the R values by supposing the following transitions to occur in solution, these transitions being brought about by diluting or raising the pH of the solution:

$$HTe_4O_{13}^- \rightarrow Te_4O_{13}^{=} \rightarrow Te_3O_{10}^{=} \rightarrow H_5TeO_6^- \rightarrow H_4TeO_6^{=}$$

$$(R = 4) \quad (R = 2) \quad (R = 1{\cdot}5) \quad (R = 1) \quad (R = 0{\cdot}5)$$

[18] J. J. BERZELIUS *Ann. Phys., Lpz.* **32,** 577 (1834); E. B. HUTCHINS *J. Amer. chem. Soc.* **27,** 1157 (1905).

An explanation of the *R*-value trend could also be advanced on the basis of the existence of the $Te_2O_7^{=}$ ($R = 1$) and the $HTeO_7^{-}$ ($R = 2$) ions, but difficulty would be encountered in the interpretation of the steady *R* value of 1·5 obtained with the more dilute solutions. One would be forced to postulate that condensation may in certain cases be brought about by dilution or by raising the pH, which appears unlikely on examination of previous work on this subject. LOURIJSEN-TEYSSEDRE[6] does maintain, however, that free telluric acid is practically uncondensed, and that the tetratellurate ion suggested by her has the formula $(HTeO_4)_4$ and is formed via the HTe_2O_7 ion as the pH of the solution is increased. No evidence in support of her views is forthcoming from the present work. The existence of the ditellurate ion in solution as an intermediate between the tri- and the mono-tellurate is not precluded, although this ion was not indicated by either the ion-exchange or the spectrographic results.

An examination of the results of spectrophotometry on solutions containing 0·14 g atoms of tellurium per litre shows that the greatest displacement of spectrograms occurs in the pH region 5–7, whereas no change occurs in the pH region 8·5–11. It would appear, therefore, that an ionic change takes place in solution at pH values below 8·5, and this could be explained by a transition from the tritellurate ion to the monotellurate ion (cf. Fig. 1). At pH values above 8·5 ion-exchange results give evidence that the non-condensed ions $H_5TeO_6^{-}$ and $H_4TeO_6^{=}$ occur in solution, and the fact that no change is observed in the spectrograms in this pH region suggests that the adsorption spectra of these ions are similar.

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LETTERS TO THE EDITORS

On the relation between bond length and hybridization. The constitution of sulphur nitride

(*Received* 7 *October* 1957)

THE variation observed in the S—S bond length is generally interpreted as due to the difference in double bond character (bond order). The bond length 2·08 Å is then considered to be the single-bond distance and 1·88 Å the double-bond distance.[1] The bond lengths found in $S_2O_6^{2-}$ (2·15 Å) and in $S_2O_4^{2-}$ (2·39 Å) are difficult to explain with this assumption. Another interpretation has been suggested by the author in a recent paper,[2] in which it is indicated that a relation may exist between

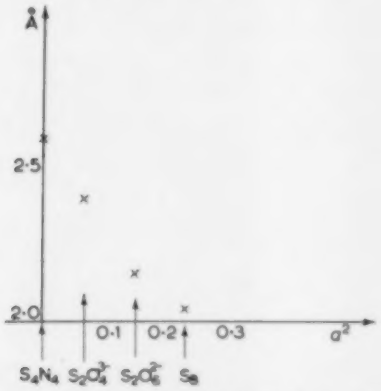

FIG. 1.—Relation between bond length and *s* character.

the *s* character of the sulphur hybrid orbitals in the σ-bond skeleton and the bond lengths. Such a discussion must in the first instance be limited to molecules and ions which are symmetrical around the S—S bond, so that the bond length can be studied as a function of only one varying *s* character (in that case identical for the hybrids from the two sulphur atoms). Fig. 1 shows the relation for $S_2O_4^{2-}$, $S_2O_6^{2-}$ and S_8. The *s* character is defined as a^2 if the normalized hybrid is written $h = a\psi_s + b\psi_p$ and orthogonal hybridization is assumed. The obvious conclusion is that a S—S bond with pure *p*-orbitals should be still longer than 2·39 Å.

Such a bond is actually found in S_4N_4, although it has not earlier been fully recognized as a single bond. The structure[3] of S_4N_4 is shown in Fig. 2. The distance between the sulphur atoms on the same side of the plane of four nitrogen atoms is as long as 2·58 Å. This distance has been explained by the use of four resonance forms, two of which contain single bonds between the sulphur atoms. CLARK[3] has pointed out that the S—S bond is approximately perpendicular to the S—N bonds. This would obviously correspond to an almost pure *p* character of the hybrid orbitals in the S—S bond.

[1] S. C. ABRAHAMS *Acta Cryst.* **7**, 423 (1954).
[2] I. LINDQVIST and M. MÖRTSELL *Acta Cryst.* **10**, 406 (1957).
[3] D. CLARK *J. chem. Soc.* 1615 (1952).

The value 2·58 Å for an *s* character = 0 has been marked out in Fig. 1 and is in good agreement with the trend indicated by the three other values.

The formula of S_4N_4 can then be written as in Fig. 3 without use of any resonance forms. An analogous but inverse formula has been suggested[4] for realgar, As_4S_4. In that case the As—As distance is as short as 2·47 Å, although it should be expected to be longer than the corresponding S—S bond in S_4N_4. The bond angle As—As—S is, however, 100° instead of 90° (in S_4N_4) and there

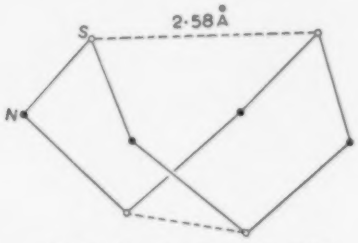

FIG. 2.—The structure of the S_4N_4 molecule.

is thus a large amount of *s* character in the hybrid orbitals in the As—As bond. The difference is thus in perfect agreement with the idea that the *s* character of the σ-bond orbitals is of importance for the bond length.

It is evidently possible to relate S—S bond lengths ranging from 2·03 to 2·58 Å directly with the *s* character of the sulphur hybrid orbitals for these symmetrical S—S bonds. This is not possible with single- and double-bond considerations. A possible extension is the conclusion that the bond lengths are mainly determined by the nature of the σ-bonds. If the *s* character corresponds to at

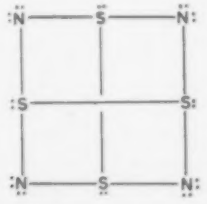

FIG. 3.—The electronic formula for the S_4N_4 molecule.

least sp^3 hybridization and there are no inert electron pairs, increasing bond order will be paralleled by increasing *s* character of the σ-bonds, and there will be a direct relation between bond length and bond order. This is the case for organic compounds. It would be important to know whether the nature of the σ-bonds or the bond order is generally the determining factor. The discussion given here for symmetrical S—S bonds is obviously purely empirical and is only a minor contribution to the study of that larger problem. It seems natural, however, that the σ-bond orbitals mainly determine the bond lengths because they are extended in the bond direction. If the bond is not symmetrical, the relation of the bond length to two different hybrid orbitals must be found. Finally, it must be pointed out that the force constants probably are more highly dependent on π-bond character than are the bond lengths.

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[4] C. S. LU and J. DONOHUE *J. Amer. chem. Soc.* **66**, 818 (1944).

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A mechanism for exchange and substitution reactions in platinum(IV) complexes

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We have found that the extremely slow exchange of chloride ion with $Pt(en)_2Cl_2^{2+}$ (*en* = ethylenediamine) is catalysed by $Pt(en)_2^{2+}$ with an attendant rate law $R = 900\ [Pt(IV)][Pt(II)][Cl^-]\ M\ min^{-1}$ at 25° in the dark. A chain mechanism involving Pt(III) postulated by Rich and Taube[1] to explain the exchange behaviour of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ is probably not applicable here, because of the rate law and because the reaction is not affected by inhibitors. However, the results can be explained in terms of the following mechanism.

$$Pt(en)_2^{2+} + Cl^- \rightleftharpoons Pt(en)_2Cl^+ \qquad (1)$$

$$\begin{matrix} en \\ en \end{matrix}\!\!>\!Pt(Cl)\!-\!Cl^{2+} + \begin{matrix} en \\ en \end{matrix}\!\!>\!Pt\!-\!Cl^+ \rightleftharpoons \begin{matrix} en \\ en \end{matrix}\!\!>\!Pt(Cl)\!-\!Cl\!-\!\begin{matrix} en \\ en \end{matrix}\!\!>\!Pt\!-\!Cl^{3+} \qquad (2)$$

A good deal of evidence for the addition of other groups to square planar complexes as suggested in (1) has accumulated recently,[2] and bridged Pt(II)—Pt(IV) halogen complexes feature often in platinum preparative chemistry.[3] Taube and King[4] have observed Cr(II) catalysis of $CrCl^{2+}$—Cl^- exchange and suggest that this occurs *via* the equilibrium:

$$Cr^{2+} + CrCl^{2+} + Cl^- \rightleftharpoons CrCl_2^+ + Cr^{3+} \qquad (3)$$

Presumably a chlorine bridge between Cr(II) and Cr(III) is formed, followed by a chlorine atom transfer. Certain two-electron redox processes are catalysed by small anions, specifically Tl(I)—Tl(III),[5] and Sn(II)—Sn(IV),[6] Sb(III)—Sb(V),[7] by halide ions. However, in these cases the rate dependencies on the concentration of halide are complex and it has been suggested that catalysis is most effective when bridging involving *two* halogens can be invoked and two halogen atoms transferred. In the platinum case the system is unique in that a Cl^+ ion must be transferred to cause exchange.

It follows from the formulation above that chloride ion should catalyse platinum exchange between the Pt(II) and Pt(IV) species and further that the rate of platinum exchange should equal the rate of chloride exchange. We have shown that a related reaction occurs rapidly in the presence of chloride

$$Pt(en)_2^{2+} + Pt(1\text{-}pn)_2Cl_2^{2+} \rightleftharpoons Pt(en)_2Cl_2^{2+} + Pt(1\text{-}pn)_2^{2+} \qquad (4)$$

ion, in which the change is followed by the optical rotation difference of 1-propylenediamine(1-*pn*) in the two complexes. Within experimental error the half-life for the change in optical rotation is equal to the calculated half-life for radio-chloride exchange in the ethylenediamine system. In the absence of chloride ion, the reaction goes, but slowly. The equilibrium constant is nearly unity for this reaction (and for the related dibromo reaction). The reaction does not occur with the dihydroxy Pt(IV) complex.

Since the ligand that adds to platinum (II) need not be the same as those attached to platinum(IV), it follows that there may be a very common mechanism for substitution reactions of Pt(IV) involving Pt(II) catalysis. Certainly this phenomenon should always be searched for when investigating the kinetics of substitution of Pt(IV) complexes.

It is intended to publish full details of this work elsewhere at a later date. This investigation was supported by a grant from the U.S. Atomic Energy Commission under contract AT(11-1)-89-project No. 2.

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[1] R. L. Rich and H. Taube *J. Amer. chem. Soc.* **76**, 2608 (1954).
[2] C. M. Harris, R. S. Nyholm and N. C. Stephenson *Nature, Lond.* **177**, 1127 (1956); C. M. Harris and R. S. Nyholm *J. Chem. Soc.* 4375 (1956).
[3] *Gmelins Handbuch der anorganischen Chemie* 68D (Pt), p. 616 *et seq.*
[4] H. Taube and E. L. King *J. Amer. chem. Soc.* **76**, 4053 (1954).
[5] G. Harbottle and R. W. Dodson *J. Amer. chem. Soc.* **73**, 2442 (1951).
[6] C. B. Amphlett *Quart. Rev.* **8**, 219 (1954); C. I. Browne, R. P. Craig and N. Davidson *J. Amer. chem. Soc.* **73**, 1946 (1951).
[7] H. M. Neumann and H. Brown *J. Amer. chem. Soc.* **78**, 1843 (1956).

BOOK REVIEWS

J. A. KITCHENER: **Ion Exchange Resins.** Methuen, London, 1956. VII + 109 pp., 9s. 6d.

THIS Methuen monograph sets out to describe the basic principles governing the behaviour of ion exchange resins and membranes. Actually it does rather more than this, for the two chapters (which occupy nearly half the book) on the physical chemistry of exchange equilibria and the kinetics of ion exchange are up-to-date and reasonably complete accounts of present theory. The writing is very concise, but the condensation has been most skilfully done, and the book will make easy reading for anyone with the necessary background of classical physical chemistry. A short list of selected references is given at the end of each chapter.

The applications of resins that are discussed are the more spectacular successes in water treatment, uranium extraction, and rare-earth and amino-acid separations; a diagram from the recent literature also shows the successful separation of the trans-uranic elements 95–101. There is, in addition, an informative table which summarizes the other possible uses of ion-exchange resins; but it is, perhaps, a pity that the author could not spare a page or two to illustrate the ubiquity of resins as tools in ordinary preparative and analytical work. In other respects the book provides an excellent guide for the non-specialist, and gives an attractively written account of the achievements and potentialities of ion-exchange resins.

C. W. DAVIES

The Chemistry of the Co-ordination Compounds. Edited by JOHN C. BAILAR, JR., Reinhold Publishing Corporation, New York, 1956. x + 834 pp. $18.50 (148s).

PROF. BAILAR is ideally suited to edit a treatise on co-ordination chemistry. He has worked many years in this research field and has stimulated many students to continue research on this subject after they completed their research training with him. He, and his former students who have joined him in writing the various chapters of this book, represent then a formidable combination.

There is an imaginative choice of topics. These include such diverse subjects as the occurrence of co-ordination compounds in natural products, as well as in the industrially important dyes and pigments, and metal carbonyls. Chapters which particularly appealed to this reviewer (probably largely dictated by his own interests) included the following: Chapter 1 (J. C. BAILAR JR. and DARYLE H. BUSCH), an interesting general account of the subject, from the point of view of the various donor atoms encountered, which cleverly introduces and refers to many of the other twenty-two chapters; Chapters 3 and 4 (ROBERT W. PARRY and RAYMOND N. KELLER), containing a well-conceived account of the theoretical basis of co-ordination binding (spiced occasionally with a little provocativeness); Chapters 8 and 9 (F. BASOLO and B. P. BLOCK respectively), dealing with the stereoisomerism of 6- and 4-covalent compounds; and finally Chapter 18 (R. C. BRASTED and W. E. COOLEY), an interesting and thorough account of the applications of physical methods to co-ordination chemistry.

In a book of such a scope (there are over 5000 literature references included) it is inevitable that important facts will have been omitted. There are no references later than 1952 included in a chapter dealing with the less common co-ordination numbers, a subject in which significant developments have occurred since that date. The limitations of JOB's Method of Continuous Variations (p. 569) and the COTTON effect (p. 581) are not emphasized, and some important developments in thermodynamic and kinetic aspects of complex ion chemistry are barely mentioned. In addition, some final

tidying up of the book as a whole could have been undertaken with advantage. For instance, two different explanations (with no suggestion of which is the more likely) are given for the rapid Co_{aq}^{3+}–H_2O^{18} exchange (pages 21 and 218), and for the existence of blue and brown forms of the diphenylmethylarsine copper complex (pages 83 and 604).

The book as a whole is, however, a thoroughly readable one, and despite some disappointing features, such as have already been mentioned, it is suggested that its availability is a must for any research worker interested in this important branch of chemistry. It contains a vast amount of useful information and will undoubtedly be the standard text in English for some time.

R. G. WILKINS

Papers to be published in future issues

MOSTAFA F. AMR EL-SAYED and RAYMOND K. SHELINE: the position of the C≡N stretching frequency in organic and inorganic molecules

A. R. FRITSCH and J. M. HOLLANDER: Radiations from decay of bismuth-203, bismuth-204, lead-204*m* and bismuth-205

J. G. CUNINGHAME: Some further fission yields in spontaneous fission of Cf^{252}

INGVAR LINDQVIST and JOHANNES WEISS: Die Kristallstruktur des Platin-Tetrathionitrosyls

J. F. ELLIS and K. D. B. JOHNSON: The fluorides of uranium—I. Liquid–vapour equilibria in the systems uranium haxafluoride–chlorine trifluoride and uranium hexafluoride–bromine pentafluoride

J. F. ELLIS, L. H. BROOKS and K. D. B. JOHNSON: The fluorides of uranium—II. Distillation of mixtures of corrosive volatile fluorides including uranium hexafluoride

JOHN D. CORBETT and PYRTLE X. SEABAUGH: Preparation of the niobium(IV) and niobium(III) iodides

VILLIERS W. MELOCHE and RONALD L. MARTIN: The alpha furildioxime complex of rhenium

W. T. CARNALL, P. R. FIELDS, D. C. STEWART and T. K. KENNAN: The absorption spectrum of aqueous curium(III)

RICHARD L. CARLIN and JOHN O. EDWARDS: The reaction of thiocyanatopentamminecobalt(III) ion with chromous ion

C. B. AMPHLETT, L. A. MCDONALD and M. J. REDMAN: Synthetic inorganic ion-exchange materials—I. Zirconium phosphate–II. Hydrous zirconium oxide and other oxides

GEORGE W. WATT and LAURIE VASKA: The interaction of ammonium and potassium hexabromoosmate(IV) and liquid ammonia at 25°—II. The ammonia-soluble products

TAICHI SATO: The extraction of uranyl nitrate from nitric acid solutions by tributyl phosphate

T. A. EASTWOOD and R. P. SCHUMAN: Curium-249

G. H. SHIFLETT, M. E. STEIDLITZ, F. D. ROSEN and W. DAVIS, JR.: The chemical effect of alpha particles on uranium hexafluoride

F. G. SHERRIF and EL-SHAMY: A study of the ferric azide reaction

ARIL K. MUKHERJI and ARUN K. DEY: Spectrophotometric and electrical conductance studies on chelate formation of uranyl ion with ammonium aurintricarboxylate

D. HALL and G. N. WALTON: Chemical effects in fission product recoil—III. The decomposition of potassium nitrate

H. A. JOHANSEN: The stoicheiometry of MnTe

ARTHUR W. ADAMSON, H. OGATA, J. GROSSMAN and R. NEWBURY: Oxalato complexes of Co(II) and Co(III)

R. A. HORNE: The ion-exchange resin adsorption of thallium(I) and (III)

ARTHUR C. WAHL: Nuclear-charge distribution in fission: cumulative yields of short-lived krypton and xenon isotopes from thermal-neutron fission of U^{235}

J. A. BROTHERS, R. G. HART and W. G. MATHERS: The nitrate complexes of tetravalent plutonium

GÜNTER HERRMANN: Über die elektrolytische Abscheidung von träger freim Strontium aus wässriger Lösung

ERNESTO GIESBRECHT and L. F. AUDRIETH: Phosphates and polyphosphates of the rare earth elements—II. Pyrophosphate and triphosphate complexes of neodymium yttrium

ILLMARS KALNIUS and GEORGE GIBSON: The interaction of uranium tetrachloride with hydrazine ammonia and amines

ROBERT E. MCCARLEY, DON S. MARTIN, JR. and LEE T. FOX: Solid state and solution exchange between $[Pt(en)Br_4]$ and $[Pt(en)Br_2]$

JOCHEN FAHLAND, GÜNTER HERRMANN and FRITZ STRASSMAN: Zur Kinetik der elektrochemischen Abscheidung radioaktiver Ionenarten auf Metallaberflächen

K. ALCOCK, G. F. BEST, E. HESFORD, and H. A. C. MCKAY: Tri-*n*-butyl phosphate as an extracting solvent for inorganic nitrates—V. Further results for the tetra and hexavalent actinide nitrates

JAROMÍR MALÝ and VÁCLAR VESELÝ: A contribution to sodium polyuranate chemistry

J. LEWIS, R. J. IRVING and G. WILKINSON: Infra-red spectra of transition metal–nitric oxide complexes-I

R. CONSTANT: Production de ^{121}I sans porteur à partir d'acide tellurique

D. G. TUCK: The properties of inorganic compounds in organic solvents—I. The hydrolysis and polymerisation of quadrivalent plutonium nitrate

D. F. C. MORRIS: Lattice energies and related properties derived using lyotropic numbers

ARTHUR C. WAHL and WILLIAM R. DANIELS: Emanating power of barium stearate for 3·9-second actinon (Rn^{219})

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RADIATIONS FROM DECAY OF BISMUTH-203, BISMUTH-204, LEAD-204*m*, AND BISMUTH-205*

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(*Received* 18 *September* 1957)

Abstract—A study has been made of the radiations from the neutron-deficient isotopes ^{203}Bi, ^{204}Bi, ^{205}Bi and ^{204m}Pb, principally by conversion electron spectroscopy with four 180° electron spectrographs of the permanent-magnet type. The decay schemes of the bismuth isotopes are found to be very complex, and in spite of high-resolution studies and some coincidence work, unique level schemes cannot be given in any case. A new transition in the decay of the 1hr ^{204}Pb isomer has been identified at 289·5 keV, and this is interpretated as arising from a 4$^+$ state of ^{204}Pb at 1563 keV. A comparison is given of the results of the present study of ^{205}Bi decay with those of other recent spectroscopic studies of the ^{205}Pb levels.

STUDIES of the electron-capture decays of the neutron-deficient bismuth isotopes have been of interest because they provide a means of observing the energy levels of corresponding lead isotopes that differ from the double-closed shell by only one or more neutrons and hence are describable in terms of the extreme single-particle model.

The decay of ^{207}Bi populates levels of ^{207}Pb, levels of a single neutron (hole) in the 126 shell. These levels are, in order of increasing energy: $p_{1/2}$, $f_{5/2}$, $p_{3/2}$, $i_{13/2}$ and $f_{7/2}$.

The levels of a neutron pair manifest themselves in ^{206}Pb, and have been studied from the electron-capture decay of ^{206}Bi by ALBURGER and PRYCE.[1] Their results indicate a marked increase in complexity of the ^{206}Pb levels over those of ^{207}Pb as evidenced by the twenty-six transitions and twelve states that are reported. An approximate theoretical treatment of the two neutron holes, originally developed by PRYCE,[2] was applied with considerable success in the interpretation and understanding of the experimental ^{206}Pb results.

This work had as its objective the study of the decays of ^{203}Bi, ^{204}Bi, and ^{205}Bi by methods of high-resolution β-spectroscopy. Subsequent to its completion, we became aware of the detailed study of ^{205}Bi by SCHMORAK, STOCKENDAL, MCDONELL, BERGSTRÖM and GERHOLM.[3] For the most part, the transition data of the two investigations of ^{205}Bi are in good agreement, although the electron–electron coincidence work by SCHMORAK *et al.* leads them to a different conclusion regarding the first excited state of ^{205}Pb from that we have reached from consideration of ^{209}Po α-decay data. We shall not present here our data on ^{205}Bi in detail, but only point out areas where further work seems necessary. A more complete description of this work is to be found in the thesis by one of us (A. R. F.).[4]

* This work was done under the auspices of the U.S. Atomic Energy Commission.
† Present address: Westinghouse Electric Corporation, Pittsburgh, Pa.
[1] D. E. ALBURGER and M. H. L. PRYCE *Phys. Rev.* **95**, 1482 (1954).
[2] M. H. L. PRYCE *Proc. phys. Soc. Lond.* A**65**, 773 (1952).
[3] M. SCHMORAK, R. STOCKENDAL, J. A. MCDONELL, I. BERGSTRÖM and T. R. GERHOLM *Nucl. Phys.* to be published (1958).
[4] A. R. FRITSCH URCL-3452, Thesis (June, 1956).

The present results on ^{203}Bi and ^{204}Bi are in no sense complete or even satisfactory. However, as further work is not being carried on presently in this laboratory on this problem, we believed that a brief summary of our experimental data would be of value, even though unique decay schemes cannot be given. Indeed, ^{204}Bi decay, with sixty-seven transitions identified, may continue to challenge nuclear spectroscopists for some time.

BOMBARDMENTS AND CHEMISTRY PROCEDURES

The bismuth activities were produced by means of α-particle bombardments upon enriched samples of ^{203}Tl (80 per cent ^{203}Tl, 20 per cent ^{205}Tl), using the Crocker 60 in. cyclotron. The energies of the α-particles were chosen in such a manner that a distinction could be made between the nuclides. To obtain the 14-day ^{205}Bi, bombardments were carried out at 28 MeV, which is below the $\alpha,3n$ threshold and yet allows the full $\alpha,2n$ yield to be obtained. ^{204}Bi and ^{203}Bi are not produced at this energy, and contamination by ^{206}Bi is held to a minimum. For study of 12-hr ^{204}Bi, bombardments of ^{203}Tl were made at 38 MeV; at this energy ^{203}Bi is not produced, but much ^{206}Bi is formed from the α,n reaction on ^{203}Tl and the $\alpha,3n$ reaction on ^{205}Tl. ^{206}Bi and ^{204}Bi are relatively easy to differentiate, however, because of the large difference in their half-lives. The 12 hr ^{203}Bi was obtained by full-energy α-bombardments at 45 MeV. Approximately equal amounts of 12 hr ^{203}Bi and 12 hr ^{204}Bi are formed at this energy, hence the assignment of transitions to ^{203}Bi could be made only after ^{204}Bi had been studied separately.

The target material, Tl_2O_3, was dissolved immediately after bombardment in a minimum volume of concentrated hydrochloric acid. Recovery of the thallium was effected by extractions with diethyl ether saturated with concentrated hydrochloric acid. The activity was adsorbed on a Dowex-1 anion-exchange column, following which the lead fraction was removed by elution with 20 ml of 0·1 N HCl. The bismuth activity was then stripped from the column with 1 N H_2SO_4, evaporated to dryness, dissolved in dilute HCl, and subsequently electroplated upon 5-mil platinum wires.

EXPERIMENTAL METHODS

Photon spectra of these isotopes were obtained by use of a NaI(Tl) scintillation detector coupled to a 50-channel analyser. Conversion-electron spectra were examined with four permanent-magnet β-spectrographs ranging in field strength from 50 G to 340 G and operating at ~0·1 per cent momentum resolution.[5] Some γ–γ coincidence experiments have also been performed.

Bismuth-203

Half-life

The half-life of ^{203}Bi was measured by following the decay of the *K*-conversion line of the 825-keV transition in the double-focusing spectrometer with the result: $t_{1/2} = 11{\cdot}5 \pm 1{\cdot}0$ hr.

Scintillation spectrum

Because of the complexity of the spectrum and because of the presence of ^{204}Bi in the samples, the photon spectrum revealed clearly only the strong transition at

[5] W. G. SMITH and J. M. HOLLANDER *Phys. Rev.* **101**, 746 (1955).

825 keV, and hence was of little value in providing information about the many other transitions from ^{203}Bi decay.

Electron spectrum

A summary of the ^{203}Bi transitions observed from the electron spectrum is given in Table 1. Eight transitions have been identified with a moderate degree of certainty by the observation of at least three conversion lines of each; seven other transitions are assigned from observation only of *K*-lines. Because our samples of ^{203}Bi were

TABLE 1.—TRANSITIONS OBSERVED FROM ^{203}Bi ELECTRON SPECTRUM

Transition energy (keV)	Relative electron-line intensities*								Probable multipole order
	K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	*N*	
60·1		vw			§			w	*M*1 ?
117·7	w†	vw			vvw?			vvw	M1 ?
126·4	vw		300	230		100	60	vvw	*E*2
186·5	1040	200			170			vw	*M*1, *M*2
264·0	770	180			vw				M1, *M*2
819·7	100	vvw							
824·9	1000	250			150				*M*4
1033·7	35	vvw							
381·5‡	100								
465·4	vvw								
606·1	50								
625·0	vw								
708·4	75								
722·1	30								
1536·4	60								

* Where the lines were too weak for densitometry, visual estimates of line blackness are given. w = weak, v = very.
† Unresolved from ^{204}Bi 105·5-keV γM_I line.
‡ The seven assignments below are tentative; only the *K*-lines have been observed.
§ M_I line masked by K–L_I–L_{II} Auger line.

weaker than the corresponding ^{204}Bi and ^{205}Bi samples, we feel that the ^{203}Bi spectrum reported here is incomplete, and that with stronger sources many more transitions will probably appear.

A multipolarity assignment can definitely be made for the 126·4-keV transition, which is identified by its *L*-subshell conversion pattern as an *E*2 transition. The 60·1, 117·7, 186·5 and 264·0-keV transitions are shown to be predominantly magnetic by their high L_I conversion, but either *M*1 or *M*2 is possible. The 824·9-keV isomeric transition has been identified as *M*4, from its half-life and its *K*-conversion coefficient.[6]

^{203}Pb isomer

This lead isomer was discovered by HOPKINS,[7] who measured its half-life as 5·6 sec and assigned it to ^{202m}Pb. The later assignment to ^{203m}Pb was made by

[6] R. STOCKENDAL, J. A. MCDONELL, M. SCHMORAK and I. BERGSTROM *Ark. Fys.* **11**, 165 (1956).
[7] N. J. HOPKINS *Phys. Rev.* **88**, 680 (1952).

FISCHER. In order to strengthen this mass assignment, we have verified the genetic relationship between this isomer and its ^{203}Bi parent by a chemical "milking" experiment. The ^{203}Bi activity was placed upon an ion-exchange column containing Dowex-1 anion resin, and ^{203}Pb was stripped rapidly from the column with a small volume of 0·1 N HCl and then placed into a counter. The entire procedure consumed about 5 sec. The "best" value of the half-life obtained from twenty-two such experiments was 7·1 $\pm$ 0·5 sec.

A continuous-flow system was also assembled so that the photon spectrum of the isomer could be examined with the scintillation spectrometer. Only one photopeak

TABLE 2

Transition-energy sums of ^{203}Bi decay

60·1	+ 126·4 =	186·5
Crossover	=	186·5
186·5	+ 819·7 =	1006·2
381·5	+ 625·0 =	1006·5
264·0	+ 824·9 =	1088·9
381·5	+ 708·4 =	1089·9
606·1	+ 824·9 =	1431·0
708·4	+ 722·1 =	1430·5

was seen, with an energy 826 $\pm$ 5 keV; this is presumably the previously identified[6] $M4$ isomeric transition of ^{203m}Pb. In a γ–γ coincidence experiment, essentially zero coincidences were observed with this photon, indicating that the isomer decays directly to the ground state. A more precise value of the transition energy, measured from the ^{203}Bi electron spectrum, is 824·9 $\pm$ 1·0 keV.

Transition sums

Although a level scheme will not be presented for ^{203}Pb, a few transition-energy sums can be noted that may be of help in establishing this scheme. These are given in Table 2, and are based upon an acceptance criterion of agreement within 0·1 per cent. The significance of sums of the transitions based on K-line assignments alone is of course questionable.

Conclusions—^{203}Bi

A possible similarity between the ^{203}Pb and ^{205}Pb energy levels is indicated by a comparison of the energies of a number of the stronger transitions of these nuclides as follows:

^{203}Pb	^{205}Pb
126·4	112·2
264·0	260·5
381·5	383·0
625·0	626·2
708·4	703·3
1033·7	1043·5

That there are fewer reported transitions of ^{203}Bi than of ^{205}Bi may be due merely to the experimental difficulty in producing ^{203}Bi in quantities comparable to ^{204}Bi and ^{205}Bi, because the thick targets that were employed have the effect of reducing the $\alpha,4n$ yields relative to those of the $\alpha,3n$ and $\alpha,2n$ reactions.

Bismuth-204 *and Lead*-204*m*

Half-life

A ^{204}Bi sample was followed for one week in a G–M counter, and a half-life value of $11{\cdot}0 \pm 0{\cdot}5$ hr was obtained. The main contaminant in the sample was 6·4-day

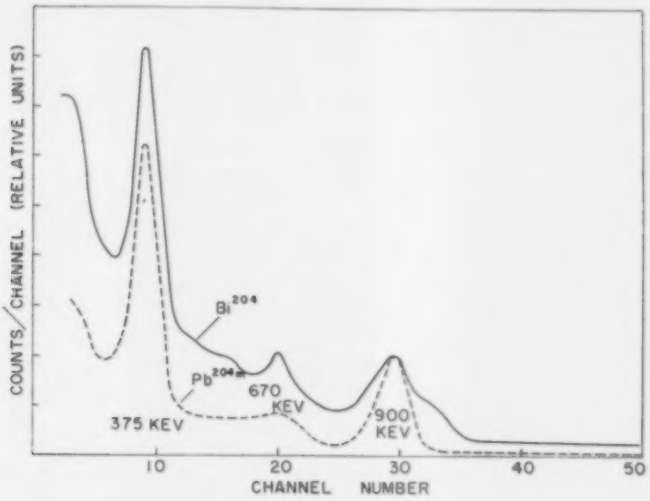

FIG. 1.—Photon spectra of ^{204}Bi and ^{204m}Pb.

^{206}Bi to the extent of 10 per cent of the initial counting rate. The bombardment had been made below the $\alpha,4n$ threshold to avoid the production of ^{203}Bi, and its absence was verified by the conversion-electron spectrum obtained with another part of the sample.

Scintillation spectrum

The photon spectrum of ^{204}Bi was obtained with the scintillation spectrometer and a comparison was made of this spectrum with that of the 68 min ^{204m}Pb isomer. The two spectra are shown in Fig. 1. The spectrum of ^{204m}Pb is known to consist only of a 375-keV photon and a pair of unresolved photons at ~900 keV. That of ^{204}Bi is evidently more complex, but the only additional photon that is easily identified is the peak at 670 keV.

Electron spectrum—^{204}Bi

The high resolution (0·1 per cent) of the permanent-magnet spectrographs was essential to a study of the extremely complex spectrum of ^{204}Bi and the associated isotopes ^{205}Bi, ^{206}Bi and ^{207}Bi. Fig. 2 shows a portion of the densitometer tracing obtained from a photographic plate of ^{204}Bi and ^{206}Bi in the energy region from 770 to 840 keV.

A listing of the transitions associated with ^{204}Bi decay is given in Table 3. These are divided into three rather subjective groups which correspond to decreasing levels of confidence in the assignments. The first and second groups contain transitions with two or more conversion lines assigned, but those in the second group are weaker or contain possible ambiguities. In the third group only one line per transition has been observed, but in at least two independent experiments. The numerical relative intensities of the stronger conversion lines have been obtained from densitometer

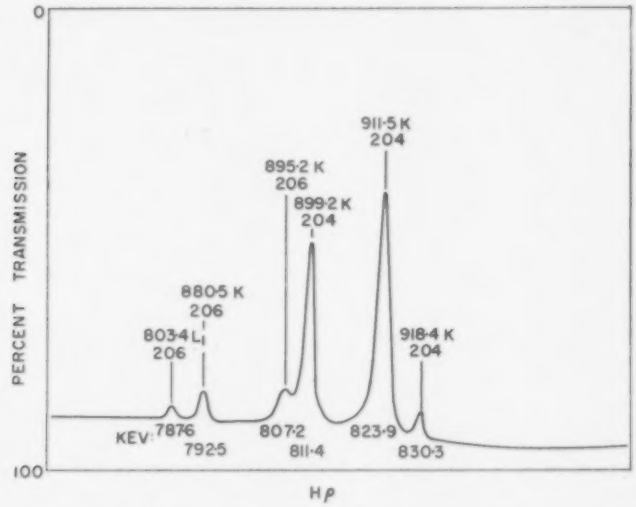

FIG. 2.—Densitometer tracing of portion of ^{204}Bi conversion electron spectrum.

tracings of the photographic spectra. The absolute accuracy of the transition energies should be better than 0·2 per cent. Relative conversion-line intensities are probably good to ±50 per cent.

Electron spectrum—^{204m}Pb

In an attempt to construct a decay scheme for ^{204}Bi one can utilize as a basic framework the simple ^{204m}Pb decay scheme. This isomer is known to de-excite by three cascade γ-rays of energies 911, 375 and 899 keV, which define levels in ^{204}Pb at 0, 899, 1274 and 2185 keV of spins and parities 0^+, 2^+, 4^+ and 9^-, respectively. We have examined the conversion-electron spectrum of ^{204m}Pb and have found a new level in ^{204}Pb which we believe lies at 1563 keV; the same conclusion has also been reached independently by HERRLANDER, STOCKENDAL, MCDONELL and BERGSTRÖM in their recent study of this isomer.[8]

The conversion electron data of ^{204m}Pb are given in Table 4. In addition to the previously known transitions, a very weak line appears which we have assigned as the *K*-line of a 289·5-keV transition; the basis for this assignment lies largely in the fact that a strong 289·5-keV transition has been identified from ^{204}Bi decay (see Table 3). Since it is not expected that there will be a new level in ^{204}Pb below the 4^+ level at 1274 keV it seems reasonable that this new level lies between the 4^+ level and the

[8] HERRLANDER, R. STOCKENDAL, J. A. MCDONELL and I. BERGSTRÖM *Nucl. Phys.* **1**, 643 (1956).

TABLE 3.—^{204}Bi TRANSITIONS

E_γ	Conversion lines observed	*K*-line intensity
78·62	$L_{II}L_{III}M_IM_{II}M_{III}N_{III}$	3080 (L_{II})
80·21	$L_IL_{II}M_IN_I$	2090 (L_I)
100·4	$L_IL_{II}M_I$	270 (L_I)
119·8	KL_I	w
140·9	KL_IM_I	1230
144·5	$KL_IM_IN_I$	m
170·0	KL_IM_I	370
176·2	KL_IM_I	1820
212·7	KL_I	90
216·2	KL_IM_I	1630
219·5	$KL_{II}L_{III}M_{II}M_{III}N_{II}$	500
222·5	$KL_IM_IN_I$	940
227·1	KL_I	80
240·7	KL_IM_I	290
249·1	$KL_IM_IN_I$	1820
289·5	KL_I	1440
291·0	KL_I	570
330·9	KL_I	170
375·0	$KL_IL_{II}L_{III}M_IN_I$	3970
405·5	KL_I	130
412·4	KL_I	120
421·8	KL_I	320
438·8	KL_I	230
501·8	KL_I	150
522·2	$KL_{II}L_{III}M_{II}$	120
532·6	KL_I	260
661·5	KL_I	210
663·4	KL_IL_{II}	80
671·0	$KL_IL_{III}M_IN_I$	810
710·4	KL_I	120
725·3	KL_I	50
791·9	KL_I	90
899·2	$KL_IL_{III}N_I$	1000
911·5	$KL_{II}L_{III}M_{II}N_{II}$	1330
918·4	KL_IM_I	110
Second confidence group		
109·1	$L_IL_{II}M_{II}$	vw (L_I)
164·9	KL_I	w
184·9	L_IL_{II}	90 (L_I)
213·5	KL_{II}	170
252·4	KL_I	80
440·2	KL_I	50
Third confidence group		
105·5	L_I	vvw
168·8	K	340
209·1	K	w
332·1	K	110
340·6	K	70
376·8	K	210
468·3	K	120
542·2	K	40

TABLE 3.—*continued*

E_γ	Conversion lines observed	K-line intensity
545·7	K	30
548·8	K	w
585·4	K	w
615·2	K	w
621·7	K	vw
646·4	K	vvw
684·3	K	vvw
718·5	K	50
745·2	K	vw
748·5	K	110
765·4	K	vw
832·3	K	40
834·3	K	50
844·1	K	100
933·6	K	vw
1056·7	K	30
1139·8	K	vvw
1203·9	K	vw
1211·5	K	vw

w = weak, m = moderate, v = very

TABLE 4.—CONVERSION LINES OBSERVED FROM ^{204m}Pb DECAY

Electron energy (keV)	Visual intensity	Assignment
201·7	vw	289·5K
287·7	vs	375·0K
359·7	m	375·0L_{II}
362·2	vw–w	375·0L_{III}
371·6	w	375·0M_{II}
374·1	vw	375·0N_{II}
811·9	vw	899·2K
824·0	ms	911·5K
896·3	m	911·5L_{II}
899·8	vw–vvw	911·5L_{III}
908·9	w	911·5M_{II}
911·6	vw	911·5N_{II}

2185-keV 9$^-$ level. We were unable to find in the ^{204m}Pb spectrum lines of a second transition corresponding to the difference between 911·5 and 289·5, i.e. 622·0 keV, but such a transition was identified in the ^{204}Bi spectrum. The 289·5-keV transition is shown to be lower in the level scheme than the 622-keV transition by two arguments:

(a) The 289·5-keV transition has a high K/L ratio (as observed in the ^{204}Bi spectrum) and hence is of low-multipole order, probably dipole. Its prominent L-conversion in the L_I subshell indicates that it is an $M1$ or an $M2$ transition and hence it could not

arise from the isomeric state, which de-excites mainly by the 911·5-keV *E*5 transition.

(b) In the ^{204}Bi spectrum, the 289·5-keV transition is very strong, whereas the 622·0 keV transition is extremely weak. It is likely, therefore, that the 289·5-keV transition lies lower in the cascade, since the alternative explanation would require that there be a very strong transition in ^{204}Bi decay that is parallel to the 622-keV transition; such a parallel transition has not been observed.

The spin of the new level, as suggested by the probable magnetic dipole character of the 289·5-keV transition, may be 3^+, 4^+, or 5^+. Analogy with the known ^{206}Pb level scheme[1] suggests an assignment of 4^+; the 622·0-keV transition would then be an *E*5, as is the 911·5-keV transition. Further demonstration of the *E*5 character of the 622·0-keV transition has been given by HERRLANDER *et al.*,[8] who find a K/L ratio of $0{\cdot}74 \pm 0{\cdot}09$, in reasonable agreement with ROSE's theoretical ratio for an *E*5 transition, 0·84.[9]

From the ^{204m}Pb spectrum, we measure the ratio of the intensity of the *K*-line of the 289·5-keV transition to that of the 375·0-keV transition as 0·027. By use of SLIV's theoretical *K*-conversion coefficient[10] for a 289·5-keV *M*1 transition (0·36), and the experimental *K*-conversion coefficient of the 375·0-keV *E*2 transition measured by HERRLANDER *et al.*[8] (0·044), we obtain a transition ratio (290/375) of 0·004. HERRLANDER *et al.* report a transition ratio (622/912) of 0·0027. Since the 622- and 290-keV transition intensities should be about equal, as well as the 912- and 375-keV intensities, these two ratios should be roughly equal. This branching may be compared with that expected theoretically from a strict E^{2L+1} dependence. The calculated ratio is $622/912 = 0{\cdot}013$, as compared with the experimental average value $622/912 = 0{\cdot}003$, indicating that the 622-keV transition is slower by a factor of about 4 (relative to the 912-keV transition) than would be predicted from the energy dependence alone.

Transition sums—^{204}Bi

To build further upon the energy-level framework provided by ^{204m}Pb, we have examined the transition-sum relationships of ^{204}Bi decay. Since there are several thousand sums obtained from the sixty-seven transitions, many accidental coincidences of sums of two transitions with other sums of two transitions will occur, even at a precision of 0·1 per cent. We have listed in Table 5, therefore, only sums of two compared with single transitions (agreement within 0·1 per cent); 111 such sums are found.

It is significant that from this list of sums the energy of the *E*5 isomeric transition, 911·5-keV, occurs as a crossover transition six times. The probability that this number of sums would occur by chance is very small, hence at least some of these cascade relationships must be significant. The six sums to $911{\cdot}5 \pm 0{\cdot}9$ keV are:

$$\begin{aligned}
832{\cdot}3 + \ 78{\cdot}6 &= 910{\cdot}9 \\
791{\cdot}9 + 119{\cdot}8 &= 911{\cdot}7 \\
671{\cdot}0 + 240{\cdot}7 &= 911{\cdot}7 \\
661{\cdot}5 + 249{\cdot}1 &= 910{\cdot}6 \\
684{\cdot}0 + 227{\cdot}1 &= 911{\cdot}1 \\
621{\cdot}7 + 289{\cdot}5 &= 911{\cdot}2
\end{aligned}$$

[9] M. E. ROSE Privately circulated tables of relativistic, screened conversion coefficients for point nuclei.
[10] L. A. SLIV Privately circulated tables of relativistic, screened K-conversion coefficients for nuclei of finite size.

TABLE 5.—ENERGY SUMS OF ^{204}Pb TRANSITIONS

Cross-over	Cascade sum		Cross-over	Cascade sum	
219·5	78·62	140·9	765·4	216·2	548·8
249·1	80·21	168·8	765·4	219·5	545·7
289·5	80·21	209·1	765·4	222·5	542·2
330·9	78·62	252·4	791·9	176·2	615·2
405·5	164·9	240·7	791·9	249·1	542·2
412·4	80·21	332·1	791·9	289·5	501·8
412·4	184·9	227·1	832·3	168·8	663·1
421·8	209·1	212·7	832·3	170·0	661·5
438·8	216·1	222·5	832·3	289·5	548·2
440·2	109·1	330·9	832·3	330·9	501·8
440·2	212·7	227·1	834·3	412·4	421·8
440·2	213·5	227·1	834·3	109·1	728·3
468·3	216·2	252·4	834·3	219·5	615·2
468·3	219·5	249·1	834·3	249·1	585·4
501·8	80·21	421·8	834·3	332·1	501·8
501·8	170·0	332·1	844·1	78·62	765·4
501·8	212·7	289·5	844·1	375·0	468·3
501·8	249·1	252·4	844·1	405·5	438·8
522·2	100·4	421·8	899·2	252·4	646·4
532·6	119·8	412·4	899·2	376·8	522·2
542·2	164·9	376·8	911·5	78·62	832·3
542·2	252·4	289·5	911·5	119·8	791·9
545·7	168·8	376·8	911·5	240·7	671·0
545·7	213·5	332·1	911·5	249·1	661·5
548·8	80·21	468·3	911·5	684·0	227·1
548·8	109·1	440·2	911·5	289·5	621·7
548·8	216·2	332·1	918·4	170·0	748·5
585·4	209·1	376·8	918·4	332·1	585·4
615·2	176·2	438·8	918·4	326·8	542·2
615·2	209·1	405·5	933·6	100·4	832·3
615·2	240·7	375·0	933·6	140·9	791·9
646·4	100·4	540·7	933·6	168·8	765·4
646·4	144·5	501·0	933·6	184·9	748·5
646·4	240·7	405·5	933·6	209·1	725·3
661·5	119·8	542·2	933·6	222·5	710·4
661·5	222·5	438·8	1056·7	213·5	844·1
661·5	249·1	412·4	1056·7	222·5	834·3
663·4	78·62	585·4	1056·7	291·0	765·4
663·4	140·9	522·2	1056·7	330·9	728·3
663·4	330·9	332·1	1056·7	332·1	725·3
671·0	168·8	501·8	1056·7	144·5	911·5
671·0	249·1	421·8	1056·7	212·7	844·1
671·0	330·9	340·6	1139·8	222·5	918·4
684·0	216·2	468·3	1139·8	240·7	899·2
710·4	164·9	545·7	1139·8	375·0	765·4
710·4	168·8	542·2	1139·8	421·8	718·5
710·4	209·1	501·8	1139·8	468·3	671·0
718·5	170·0	548·0	1203·9	412·4	791·9
718·5	176·2	542·2	1203·9	438·8	765·4
718·5	216·2	501·8	1203·9	532·6	671·0
725·3	78·62	646·4	1203·9	542·2	661·5
728·3	176·2	548·8	1211·5	376·8	834·3
745·2	212·7	532·6	1211·5	501·8	710·4
745·2	222·5	522·2	1211·5	548·8	661·5
745·2	332·1	412·4	1211·5	548·8	663·4
748·5	216·2	532·6			

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Only one of these six pairs of cascade transitions has actually been observed in the electron spectrum of the isomer itself (by HERRLANDER *et al.*[8]), therefore one must account for the absence of the other cascades on intensity grounds if the sum are to be considered valid.

Two sums that can clearly be rejected in this way are those of the 240·7–671·0 pair and the 661·5–249·1 pair, because the *K*-lines of all these transitions are much too intense in the ^{204}Bi spectrum to have been unobserved in the ^{204m}Pb spectrum. The status of the other three ^{204}Bi sums remains in question, because at least one of each pair is sufficiently weak relative to the 911·5 that it could have been missed in the ^{204m}Pb spectrum. It would be desirable to re-examine the ^{204m}Pb spectrum with stronger sources to search for these weak competing isomeric transitions.

Conclusions—^{204}Bi

A ^{204}Pb level scheme cannot be constructed on the basis of the numerical sum relationships alone; the complexity is such that a precision greater than 0·1 per cent would be required. Electron–electron coincidence work at fairly high resolution could also help to decide the true or accidental nature of some of the transition sums.

Bismuth-205

Half-life

A sample of ^{205}Bi was followed for more than seven half-lives with a G–M counter to obtain a value for the ^{205}Bi half-life of 15·3 $\pm$ 0·7 days. Approximately 80 per cent of the initial counting rate of the sample was ^{205}Bi; the other 20 per cent was 6 day ^{206}Bi with a very small amount of 8 year ^{207}Bi.

TABLE 6.—^{205}Bi PHOTON SPECTRUM

Energy of γ-ray (keV)	Relative intensity
570	0·35
700	1·00
1000	0·62
1770	2·0

Scintillation spectrum

The γ-ray scintillation spectrum of ^{205}Bi was examined for a measure of the relative intensities of the more intense photons; the results are given in Table 6.

Electron spectrum

The transitions assigned to ^{205}Bi decay from this work, and from the work of SCHMORAK *et al.*,[3] are given in Table 7. Also given are the measured intensities of various prominent lines relative to the *K*-line of the 703·3-keV transition. The agreement of the transition energies with those reported by SCHMORAK *et al.*[3] is for the stronger transitions very good.

TABLE 7.—TRANSITIONS OBSERVED IN ^{205}Bi DECAY

E_γ (keV)		I (K-line)	
This work	SCHMORAK *et al.*	This work	SCHMORAK *et al.*
112·2	—	11·5 (*L*)	—
—	115·2	—	10 (*L*)
131·2	—	—	—
149·0	—	—	—
192·6	—	—	—
—	235·9	—	8
260·5	260·5	83	110
282·4	282·3	33	41
284·0	284·2	116	160
349·3	349·4	29	28
383·3	383·2	—	6
493·5	493·6	11	11
511·7	511·7	16	22
526·0	—	—	—
531·1	—	—	—
550·3	550·0	—	6·3
570·7	571·0	77	74
573·7	—	—	—
579·7	580·0	26	24
626·2	626·5	—	6·7
—	688·9	—	1
703·3	703·3	**100·0**	**100·0**
744·6	745·0	—	2·1
758·6	758·3	—	3·1
—	761·0	—	2·0
910·7	910·8	—	9·8
987·5	987·8	21	27·5
—	1002·7	—	2·1
1014·0	1014·2	—	4·9
1043·5	1043·7	22	32·5
1073·3	—	—	—
1190·1	1190·3	—	7·6
~1346	1337	—	0·3
—	1351·5	—	1·1
—	1502·5	—	0·4
—	1552·0	—	0·8
~1617	1614·6	—	3·1
—	1766·4	—	43·6
—	1777·4	—	5·2
—	1863·3	—	2·0
—	1906·5	—	0·6
—	~2600	—	<0·5

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γ–γ Coincidences

Because of the complexity of the ^{205}Bi spectrum, little information was gained from γ–γ coincidence experiments. The only certain results were that the 570-keV transition is in coincidence with the 1044-keV transition and that the 703-keV transition is in coincidence with radiation of energy greater than 1750 keV.

A search was also conducted for delayed states in ^{205}Bi decay. By gating with the *K* X-rays and comparing the resulting coincidence spectrum with the singles spectrum, one was able to discern that none of the more intense transitions was delayed, since both spectra were almost identical. By gating on the *K* X-rays and inserting appropriate delays into the coincidence circuit, an upper limit of about 5×10^{-9} sec was set on the half-life of the 703-keV *E*2 γ-ray. A similar limit was set for the other transitions.

Search for isomeric state in ^{205}Pb

Since isomers of the *M*4 type are known to occur in ^{201}Pb, ^{203}Pb and ^{207}Pb, it has been expected that ^{205}Pb should also have such an isomer. Further, the ^{203}Pb and ^{207}Pb isomers are directly populated to a considerable extent from the decay of ^{203}Bi and ^{207}Bi, respectively; hence it was natural to search for the ^{205}Pb isomer from the decay of ^{205}Bi.

From the known half-lives of ^{207m}Pb (0·8 sec) and ^{203m}Pb (7 sec), one predicts a half-life of from 1·5 to 2 sec for a similar *M*4 isomer in ^{205}Pb. Also an interpolation of the energies of the ^{207}Pb and ^{203}Pb isomeric transitions leads to a prediction of an energy of 900–1000 keV for the ^{205}Pb isomer.

We have searched for this isomer, in two separate experiments, with negative results. The experimental method was the following: Sources of fairly pure ^{205}Bi were produced by α-particle bombardment of ^{203}Tl well below the α,3*n* threshold. The regular chemical procedure was followed, except that in the final step the bismuth activity was allowed to remain upon the anion-exchange column. A continuous-flow system with 0·1 N HCl as eluant was then used to remove the lead-daughter activity continuously and pass it along a glass tube at a known flow-rate. By means of a single-channel scintillation spectrometer the activity could be measured as a function of distance along the glass tube, and hence the half-life determined.

The experiment yielded a half-life of 0·7 sec, which agrees with the known half-life of ^{207m}Pb (0·8 sec). Further proof that this activity was ^{207m}Pb was obtained by identification in the γ-spectrum of the 570-keV γ-ray of ^{207m}Pb.

It is possible from these experiments to set an upper limit to the population of such a ^{205}Pb isomer by the decay of ^{205}Bi, using the figure of 90 per cent for the population of ^{207m}Pb by ^{207}Bi decay and the known half-lives of ^{207}Bi (8 years) and ^{205}Bi (15·3 days). Assuming that the ^{203}Tl(α,2*n*)^{205}Bi cross-section is about the same as the ^{205}Tl(α,2*n*)^{207}Bi cross-section, and knowing the isotopic enrichment of the thallium target material, one calculates that the population of an isomeric state in ^{205}Pb by decay of ^{205}Bi is less than 0·1 per cent. This limit, of course, is valid only for an isomer similar to that of ^{203m}Pb and ^{207m}Pb; an isomer with half-life less than 0·3 sec is not ruled out by these experiments.

Transition-energy sums and level scheme

On the basis of transition-energy sums and coincidence information, SCHMORAK *et al.*[3] have presented a level scheme of ^{205}Pb in which ten levels were considered to

be well established. These levels were given, in keV, as: ground, 282·3, 703·3, 987·6, 1043·7, 1614·6, 1705·4, 1766·4, 2054·8 and 2566·5. Because of the close agreement of our transition energies with those of SCHMORAK *et al.*, most of the sum relations are also in accord. There is, however, recent information obtained from studies of the

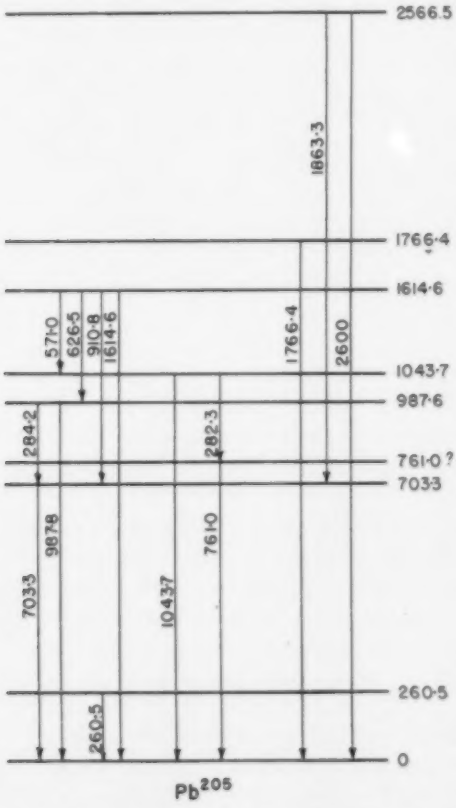

FIG. 3.—Partial level scheme of ^{205}Pb (energies are those of SCHMORAK *et al.*).

α-decay of ^{209}Po which is in contradiction to the above level order. ASARO and PERLMAN[12] have found that the first excited state of ^{205}Pb lies at 260 ± 2 keV rather than at 282·3 as postulated by SCHMORAK *et al.* It appears, therefore, that the 260·5-keV transition (see Table 7) must be placed lowest in the scheme. Although much uncertainty remains in the ^{205}Pb level order, we show in Fig. 3 a revision of part of the level scheme of SCHMORAK *et al.* in which the energy of the first excited state has been changed* from 282·3 to 260·5 keV. Some of the difficulties with this revised scheme are the following: (1) It has not been proved that the 260 ± 2-keV transition found from ^{209}Po α-decay is identical to the 260·5-keV transition found by ourselves and by SCHMORAK *et al.* from ^{205}Bi decay. From conversion coefficient information,

* M. SCHMORAK, in a private communication, has withdrawn 282·3 keV as the energy of the first excited state.

ASARO and PERLMAN[11] consider the ^{209}Po transition to be magnetic dipole, yet the low K/L ratio observed by SCHMORAK *et al.* (3·4 ± 0·6) indicates that the transition observed from ^{205}Bi decay is $M2$. A precise energy measurement or K/L determination of the ^{209}Po transition would be most desirable. (2) The fact that coincidences were observed[3] between the 260·5 and 571·0-keV transitions is not consistent with the

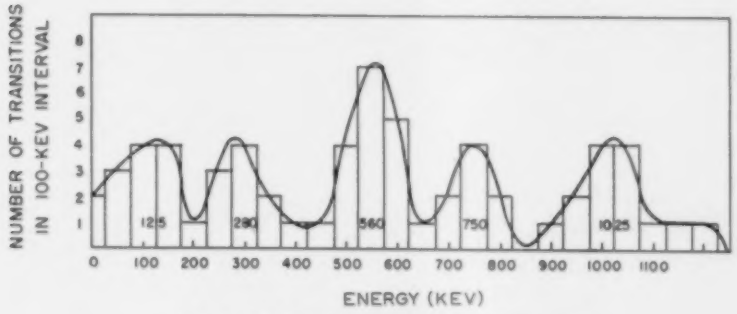

FIG. 4.—Statistical plot of ^{205}Bi transition energies.

scheme of Fig. 3. The 571·0-keV transition is known to feed the 1043·7-keV level, but because no transition (of 783·2 keV) has been observed between this level and the 260·5-keV level, the 260·5 and 571·0-keV transitions should therefore not appear in coincidence. (3) The 260·5-keV level does not appear to be populated from any higher level, but must receive all its population by direct ^{205}Bi decay. With such a profusion of higher states available, it seems strange that none of them would appreciably populate the first excited state. (4) SCHMORAK *et al.* report coincidences between the 282- and 284-keV transitions; however, the coincidence effect is very weak.

Conclusions—^{205}Bi

Because of the large number of transitions found in ^{205}Bi decay, it is interesting to observe from a statistical plot of transition energies whether or not any correlations can be made with the known energies of single-neutron transitions in this region. In Fig. 4 we give such a plot, which shows the following maxima and a possible interpretation. Apparently in the "three-hole" nucleus ^{205}Pb, manifestations of odd-nucleon transitions remain, superimposed upon the various excitations of the other nucleon pair.

Maximum (keV)	Single-neutron transition in ^{207}Pb (keV)	
125	—	
280	$p_{3/2} \rightarrow f_{5/2}$	300
560	$f_{5/2} \rightarrow p_{1/2}$	570
750	$p_{3/2} \rightarrow p_{1/2}$	870
1025	$i_{13/2} \rightarrow f_{5/2}$	1063

[11] F. ASARO and I. PERLMAN Private communication.

Acknowledgements—Thanks are due Prof. J. O. RASMUSSEN and I. PERLMAN for their comments and suggestions, and to Drs. D. STROMINGER, W. G. SMITH and F. S. STEPHENS for help with various phases of the experimental work. We are also grateful to Dr. W. W. TRUE for interesting discussions of this problem, and to Dr. M. SCHMORAK for his helpful comments.

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SOME FURTHER FISSION YIELDS IN SPONTANEOUS FISSION OF ^{252}Cf*

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(*Received* 19 *September* 1957)

Abstract—Six new fission yields have been measured on the wings of the ^{252}Cf spontaneous fission curve. The width of the peaks at half maximum height is found to be 13 ± 1 mass units.

1. INTRODUCTION

A FISSION yield curve for the spontaneous fission of ^{252}Cf was published by GLENDENIN and STEINBERG[1] in 1954. On a source of ~15 × 10^3 fissions/min of ^{252}Cf becoming available, the author decided to measure a few fission yields on both wings of the curve, since these had not been done by the previous authors. There was insufficient ^{252}Cf for any measurements to be made in the trough.

2. EXPERIMENTAL

The Cf was purified by standard radiochemical methods from the particular element whose fission yield was being measured, and the time of last separation of the Cf from the element was taken as the beginning of the growth period. After allowing the element to grow for the required time, it was separated from the Cf, purified, and mounted by the standard methods. All sources were counted by a proportional flow counter whose background was ~2 counts/min. The initial count rates of the sources varied from 10 to 100 counts/min. Counting corrections were taken from the work of FLYNN.[2]

The zirconium, molybdenum, praseodymium, neodymium and samarium samples were purified as described by CUNINGHAME.[3] For mass 101 a new fast procedure was developed in which the molybdenum fission yield was found by purifying and mounting the technetium daughter. This procedure was as follows:

(1) The Cf sample was shaken with diethyl ether to extract Mo, as was done by WILES and CORYELL[4] in their preparation of sources of ^{101}Mo. This ether extraction was repeated three more times and the time of the last phase separation was taken as the beginning of the irradiation. Mo and Fe carriers were then added.

(2) At the end of the growth period, Mo (+Tc) was extracted into ether, washed and back-extracted into water.

(3) Ferric hydroxide was then precipitated, the solution acidified, Re carrier as holdback for Tc added, and Mo precipitated with α-benzoin oxime, care being taken that this precipitation did not occur until 10 min from the Mo–Cf separation in order to allow all ^{105}Mo to die out.

* Work performed at Argonne National Laboratory under the auspices of the U.S. Atomic Energy Commission.

[1] L. E. GLENDENIN and E. P. STEINBERG *J. inorg. nucl. Chem.* **1**, 45 (1955).
[2] K. F. FLYNN Unpublished work at Argonne National Laboratory.
[3] J. G. CUNINGHAME *J. inorg. nucl. Chem.* **4**, 1 (1957).
[4] D. R. WILES and C. D. CORYELL *Phys. Rev.* **96**, 696 (1954).

TABLE 1.—FISSION YIELDS FOR THE SPONTANEOUS FISSION OF ^{252}Cf

Mass number	Element	Fission yield (%)
97	Zr	2·1 ± 0·3
99	Mo	3·0 ± 0·45
01	Mo (through Tc daughter)	4·1 ± 0·8
143	Pr	7·4 ± 1·5
147	Nd	4·0 ± 0·8
153	Sm	1·3 ± 0·3

(4) The Mo was dissolved in 6 N NaOH, Re carrier added and the ^{101}Tc allowed to grow for 22 min, then the Mo was reprecipitated with α-benzoin oxime, the Mo being reserved for a later chemical yield determination.

(5) After carrying out a rapid Mo scavenge, the solution was practically neutralized and Tc was precipitated on the Re with tetraphenylarsonium chloride.

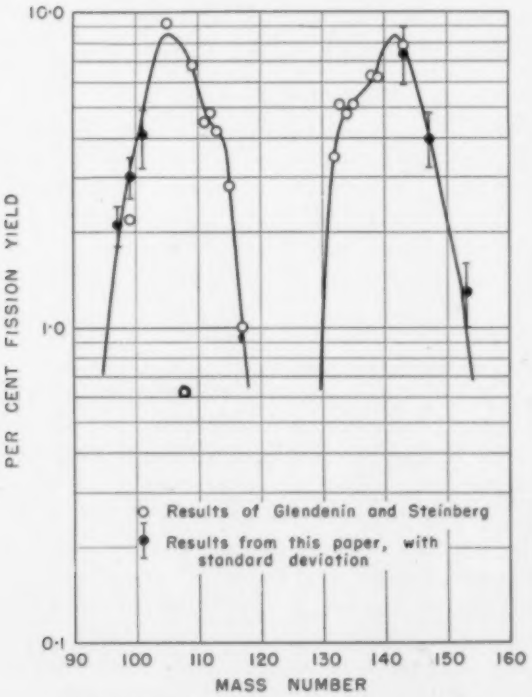

FIG. 1.—Mass-yield curve for ^{252}Cf spontaneous fission.

RESULTS

Table 1 gives the fission yields obtained, while Fig. 1 shows the fission yield curve for ^{252}Cf with the points obtained by GLENDENIN and STEINBERG,[1] and the six new points on the wings obtained in the course of this work. For the inside edges up to the peaks, the curve has been drawn as by GLENDENIN and STEINBERG, but the wings have

been obtained by drawing the best curve through the new points. Independent daughter yields are negligible in all cases.

3. DISCUSSION

The six new points are sufficient to define the wings of the ^{252}Cf spontaneous fission yield curve with reasonable accuracy. The peak width at half maximum peak height is found to be about 12 for the light peak and about 14 for the heavy. This is, however, rather sensitive to the method of drawing the curve on the inner edges, and it would perhaps be reasonable to say that this width is 13 ± 1 mass units on both peaks. This compares with a value of 13 also found by STEINBERG and GLENDENIN[5] for the width of the peaks in ^{242}Cm spontaneous fission.

Acknowledgements—The author would like to thank Drs. E. P. STEINBERG and L. E. GLENDENIN for helpful discussions, and Dr. P. R. FIELDS for supplying the ^{252}Cf. He would also like to thank Miss SYLVIA ARCHER for helping with the routine counting of the sources.

[5] E. P. STEINBERG and L. E. GLENDENIN *Phys. Rev.* **95,** 431 (1954).

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DIE KRISTALLSTRUKTUR DES PLATIN-TETRATHIONITROSYLS

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(*Received* 31 *October* 1957)

Abstract—The crystal structure of $Pt(SN)_4$ has been determined. The dimensions of the monoclinic unit cell are $a = 8{\cdot}57$ Å, $b = 7{\cdot}69$ Å, $c = 11{\cdot}14$ Å and $\beta = 101{\cdot}6°$. The space group is $P2_1/c$. The $Pt(SN)_4$ molecule is planar with two S_2N_2 chains in *cis*-position acting as bidentate ligands.

DIE Thionitrosylkomplexe mit Elementen der 8.Nebengruppe wurden erstmals von M. BECKE-GOEHRING und Mitarbeitern dargestellt.[1,2] In den ersten Veröffentlichungen wurde auch die mögliche Konstitution dieser Verbindungen diskutiert.[3,4] Die diskutierten Strukturen waren jedoch nur hypothetisch, und eine sichere Klärung auf rein chemischem Wege schien nicht möglich. Frau Prof. M. BECKE-GOEHRING schlug uns deshalb vor, die Struktur in Uppsala zu untersuchen. Die jetzt endgültig bestimmte Struktur ist früher nicht vorgeschlagen worden.

EXPERIMENTELLES

Die Verbindung wurde nach FLUCK, GOEHRING und WEISS[5] dargestellt. Für die Röntgenaufnahmen wurde ein prismatischer Kristall mit einem Durchmesser von 0,1 mm verwendet.

Es wurden Drehkristall- und Weissenberg-Aufnahmen um die *b*-Achse mit Mo-*K* Strahlung aufgenommen.

Die Gitterkonstanten sind $a = 8{,}57$ Å, $b = 7{,}69$ Å, $c = 11{,}14$ Å und $\beta = 101{,}6°$. Die früher angegebene Dichte 2,9 ist offenbar zu niedrig; denn 4 $Pt(NS)_4$ in der Elementarzelle entspricht eine Dichte von 3,5. Bei einer Neubestimmung wurde der Wert 3,4 gefunden. Die integralen Auslöschungen der Reflexe $0k0$ für $k = 2n + 1$ und $h0l$ für $l = 2n + 1$ bestimmen die Raumgruppe als $P2_1/c$.

Die Intensitäten wurden visuell geschätzt und nach LU[6] wurden relative $|F|^2$-Werte berechnet.

Eine Korrektur für die Absorption, die in diesem Falle trotz Verwendung von Mo-Strahlung beträchtlich ist, wurde nicht gemacht. Die Atomabstände sind deshalb nicht sehr genau bestimmt.

STRUKTURBESTIMMUNG

Zunächst wurden die Patterson-Funktionen $p(x,z)$ und $p(y,z)$ berechnet. (Alle Fourier-Berechungen wurden auf der HÄGG–LAURENT Maschine[7] ausgeführt.) Die Lage der Platinatome konnte hieraus leicht bestimmt werden. Eine grosse Anzahl der

[1] M. GOEHRING *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen.* Berlin (1957).
[2] M. GOEHRING *Quart. Rev.* **10**, 437 (1956).
[3] M. GOEHRING und A. DEBO *Z. anorg. Chem.* **273**, 319 (1953).
[4] K. W. DAUM, M. GOEHRING und J. WEISS *Z. anorg. Chem.* **278**, 260 (1955).
[5] E. FLUCK, M. GOEHRING und J. WEISS *Z. anorg. Chem.* **287**, 51 (1956).
[6] C. S. LU *Rev. sci. Instrum.* **14**, 331 (1943).
[7] G. HÄGG und T. LAURENT *J. sci. Instrum.* **23**, 155 (1946).

Vorzeichen der $F(khl)$ war durch die Platinbeiträge sicher bestimmt, und mit diesen Werten wurde eine dreidimensionale Elektronendichtefunktion berechnet. Das ebene PtN_4S_4-Molekül konnte leicht identifiziert werden, obwohl die Funktion einige Abbruchsmaxima von der selben Grössenordnung wie die Stickstoffmaxima aufwies. Nun konnten die Vorzeichen aller $F(hkl)$ berechnet werden, und hiermit wurde eine erneute Berechnung durchgeführt, sowie auch ein Versuch zur "Backshift" Korrektur. Die Struktur konnte durch eine vollständige Identifizierung der Abbruchsmaxima sichergestellt werden. Die Form der Maxima war aber nicht gut genug definiiert, um eine genaue Verfeinerung zu gestatten. Die folgenden Parameter wurden direkt aus der endgültigen Elektronendichtefunktion erhalten:

	x	y	z
Pt	0,054	0,167	0,636
S_I	0,904	0,299	0,473
S_{II}	0,688	0,092	0,572
S_{III}	0,279	0,296	0,611
S_{IV}	0,371	0,084	0,815
N_I	0,838	0,046	0,665
N_{II}	0,721	0,228	0,473
N_{III}	0,176	0,042	0,786
N_{IV}	0,389	0,206	0,704

Die berechneten Strukturfaktoren ergeben einen R_1-Wert von 0,17, was als befriedigend angesehen werden kann.

DISKUSSION DER STRUKTUR

Die Struktur ist in Abb. 1(a) und (b) beschrieben. Die Atomabstände und Bindungswinkel in einem Molekül sind in Abb. 2 (a) und (b) gegeben.

Die Packung der ebenen Moleküle entspricht ungefähr der berechneten Summe der van der Waalsradien bei Berührung: S—N ~3,3–3,5 Å und S—S ~3,5–3,6 Å. Einige Abstände sind bis zu 0,3 Å grösser, aber die geringe Genauigkeit mag dafür verantwortlich sein. Die Wasserstoffatomlagen können natürlich nicht festgelegt werden, und der Vorschlag von PIPER,[8] dass noch ein Paar Wassenstoffatome pro Molekül gebunden sind, kann deshalb nicht geprüft werden.

Man sollte annehmen, dass die Atomabstände und Bindungswinkel in jeder der beiden Hälften der Moleküle fast identisch sein müssten. Unsere Werte zeigen grosse Unterschiede, und wir nehmen an, dass diese Abweichungen eine geringe Genauigkeit andeuten. Es ist aber auffallend, dass das Molekül vollständig eben gefunden wurde. Die Winkelsummen der zwei Molekülhälften sind 539,8° und 540,2° (theoretisch 540°) und die Winkelsumme um Pt ist 360,2° (theoretisch 360°). Diese Ergebnisse weisen darauf hin, dass die grossen Parameterfehler nur in der Ebene des Moleküls auftreten. Hoffentlich werden diese Fragen durch die Untersuchung der $Ni(SN)_4$ beantwortet, wo man die Stickstofflagen wohl besser bestimmen kann.

Es ist wohl offenbar, dass unsere Ergebnisse keine weitgehende Diskussion der chemischen Bindung auf Grund der Bindungsabstände gestattet. Die ebene Struktur deutet aber auf eine teilweise Delokalisierung der Valenzelektronen hin, so dass wir in der Molekülebene ein σ-Bindungsgerüst haben und senkrecht darauf neun atomare

[8] T. PIPER Private Mitteilung.

p-Eigenfuktionen, die nach der Methode der Valenzstrukturen oder der Molekülzustände behandelt werden können. Einer von uns (WEISS[9]) hat in einer vorläufigen Mitteilung einige Mesomeriemöglichkeiten angegeben. Eine Behandlung mit der Methode der Molekülzustände wird gegenwärtig von Lindqvist ausgearbeitet.

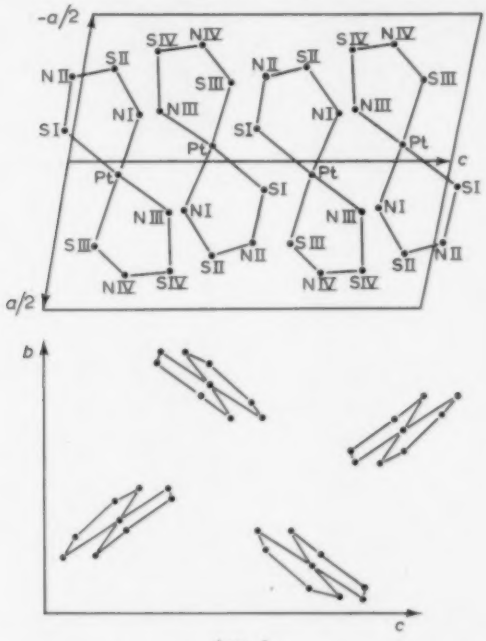

ABB. 1.
(a) Projektion der Struktur auf die *ac*-Ebene.
(b) Projektion der Struktur *senkrecht* auf die *bc*-Ebene.

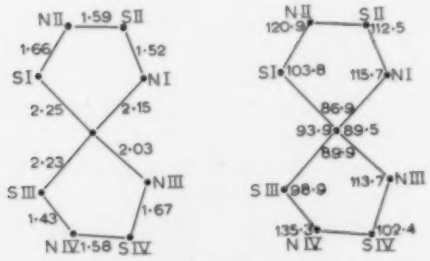

ABB. 2.
(a) Atomabstände in $Pt(SN)_4$.
(b) Bindungswinkel in $Pt(SN)_4$.

Die Deutsche Forschungsgemeinschaft unterstützte diese Arbeit durch Vergebung eines Stipendiums an den einen von uns (J. W.). Die Arbeit wurde auch von dem Schwedischen Forschungsrat der Naturwissenschaften unterstützt. Diese Hilfe wird mit Dankbarkeit anerkannt.

Wir danken auch Frau Professor BECKE-GOEHRING für Ihre freundliche Interesse und Professor HÄGG für ausgezeichnete Arbeitsmöglichkeiten.

[9] J. WEISS *Angew. Chem.* **69**, 108 (1957).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 187 to 193. Pergamon Press Ltd., London

THE POSITION OF THE C≡N STRETCHING FREQUENCY IN ORGANIC AND INORGANIC MOLECULES*

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(*Received* 26 *May* 1957; *in final form* 25 *November* 1957)

Abstract—The C≡N stretching frequency of eight inorganic cyanides is given. The position of the CN frequency in organic and inorganic molecules and ions is discussed in terms of resonance with structures containing C=N groups. In organic nitriles, the contribution of these structures is discussed in terms of the inductive and/or the mesomeric effects. In simple inorganic cyanides of metals in the same subgroup of the Periodic Table, this contribution is linearly related to the electronegativity of the central atom. In complex cyanides, on the other hand, the contribution depends on other factors such as the co-ordination and oxidation numbers of the central atom and its tendency to be positive, negative or neutral.

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COMPOUNDS containing the carbonyl group have been the subject of many theoretical and experimental investigations. However, compounds containing the isoelectronic nitrile group have not been similarly investigated. It is the purpose of this paper to indicate that conclusions similar to those obtained for carbonyl compounds can also be deduced for molecules or ions containing the nitrile group.

As in the case of the carbonyls,[1] resonance between covalent and ionic forms is to be expected:

$$-C\equiv N \leftrightarrow -\overset{+}{C}=\overset{-}{N} \qquad (1)$$

The relative contribution of the ionic form can be used to explain the position of CN frequency in both organic (2250–2225 cm^{-1}) and inorganic (~2100 cm^{-1}) compounds. This contribution increases when the CN is attached to a group or an atom with lower affinity for the electrons than the CN itself; or when the CN is conjugated with an unsaturated group or an atom with an available pair of electrons. This contribution would tend to decrease the CN force constant and, consequently, the CN frequency.

(1) *Organic nitriles*

In order to discuss the CN frequency in organic compounds one must consider:

(a) The inductive effect (±I) of an adjacent or very close group to the CN group, and/or

(b) The mesomeric effect (±M) of a group attached to the CN group or the presence of a system conjugated with it.

(a) *The inductive effect.* In the carbonyl compounds, it is well known that groups with +I effect (electron-repelling groups) decrease the carbonyl frequency because

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† From portions of a thesis to be submitted by M.F.A.E. to the Graduate School of the Florida State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[1] A. D. WALSH *Trans. Faraday Soc.* **42**, 561 (1946).

of the greater contribution of the polar $>\overset{+}{C}—\overset{-}{O}$ structure. Groups with $-I$ effect (electron-attracting groups) have an opposite effect. The same conclusions can be drawn for compounds containing the CN group by looking at Table 1. It shows that the CN frequency of different compounds—obtained under the same conditions—is very sensitive to the nature of the attached group. Generally, compounds with $-I$ groups have a higher CN frequency than those with $+I$ groups attached to the same position with respect to the CN group (compare B and D or B and E). Also, the frequency is sensitive to the inductive power of the group and its effect decreases as we go further away from the CN group (compare D and F, E and G, and H and K). In comparing the CN frequencies of the dinitriles, it is better to consider the effect of one nitrile group on the other. Since there is no conjugation, the nitrile group operates with only a $-I$ effect. If we compare compounds (D) and (H), we find that the latter exhibits a higher CN frequency. Since chlorine has the same electronegativity as nitrogen, the higher frequency in (H) is expected from the greater mobility of the π-electrons. Consequently, this kind of polarization increases the $-I$ power of the CN compared to CH_2Cl, with a subsequent increase of the CN frequency. Compound (L) has a lower frequency than (J) because of the $+I$ effect of the methyl group.

TABLE 1.—THE CN FREQUENCY OF SOME ORGANIC NITRILES[2,3]

Formula	CN frequency (cm^{-1})	Formula	CN frequency (cm^{-1})
A. $H_3C—CN$	2254	I. $NC—C—C—CN$	2261
B. $H_3C—C—CN$	2249	J. $NC—C—C—C—CN$	2254
C. $HO—C—C—CN$	2256	K. $NC—C—C—C—C—CN$	2248
D. $Cl—C—C—CN$	2260	L. $NC—C—C(CH_3)—C—CN$	2247
E. $Br—C—C—CN$	2258		
F. $Cl—C—C—C—CN$	2253	M. $Cl—CN$	2201
G. $Br—C—C—C—CN$	2252	N. $Br—CN$	2187
H. $NC—C—CN$	2278	O. $I—CN$	2158

Using the available relative electronegativities of the different groups,[4] all of the observations involving these groups can be explained. The relative electronegativities of the groups in Table 1 are:

$$CN \gg CH_3 > C_2H_5$$

Since the CN is the most electronegative one and since nitrogen is more electronegative than carbon, there would be a tendency for the polarization of the π-electrons. This gives rise to more contribution of the ionic form. This tendency would decrease and the CN frequency should increase, the closer the electronegativity values of the attached groups are to that of the CN. This explains why $\nu_{II} > \nu_{II}$

[2] Compounds A–L: R. E. KISTON and N. E. GRIFFITH *Analyt. Chem.* **24**, 334 (1952); The wavelength accuracy is $\pm 0{\cdot}5\ cm^{-1}$ (private communication).
[3] Compounds M–O: Raman Shifts W. G. PENNY and G. B. SUTHERLAND *Proc. roy. Soc.* **156**, 654 (1936).
[4] H. O. PRITCHARD and H. A. SKINNER *Chem. Rev.* **55**, 769 (1955).

and $\nu_A > \nu_B$. From ν_D, ν_E and ν_I, it is predicted that the CN has about the same electronegativity value as the chlorine, but a little bit higher than bromine.

(b) *Conjugation and mesomeric effects.* The most intensive study of nitriles confirming the existence of resonance with structure containing C≡N group is that of KITSON and GRIFFITH.[2] These workers found that in thirty-four saturated mono- and di-nitriles (excluding malonitrile) the C≡N frequency lies between 2260 and 2240 cm^{-1}, and in seventeen additional unsaturated but not conjugated nitriles the frequencies were within the same range. Twelve further nitriles in which the C≡N was conjugated with a double bond (excluding fumaronitrile) have a strong band between 2232 and 2218 cm^{-1}, and four compounds with nitrile groups of both types exhibit both absorptions. Similarly, with aromatic compounds, those in which the C≡N groups were separated from the ring by methylene groups, showed the normal frequencies of 2254 and 2248 cm^{-1}.

In order to examine the mesomeric effect, X—CN is chosen as an example (where X represents a halogen atom). In these compounds the halogen atom operates with the opposing −I and +M effects. The low values of the CN stretching frequencies of these compounds (M, N, O), as compared to the frequencies of compounds (D, E, F and G), which are shown in Table 1, indicates that the +M effect of the halogens is greater than their −I effect, since the resulting effect decreases the CN frequency. One can reach the same conclusion by comparing the force constants of the two bonds in X—CN with the corresponding bonds in compounds when the potential conjugation with the CN group does not exist. It is found,[5] that the force constant of the X—C bond is greater in X—CN than that in $X—CH_3$, whereas that of the CN is less than that in HCN.

(2) *Inorganic cyanides*

The nitrile frequency in inorganic cyanides is low compared to that in organic nitriles. This indicates that the contribution of the ionic form in the resonance hybrid in inorganic nitriles is greater than in organic nitriles. This is due to the ionic nature of the metal carbon bond in the case of the former.

Two kinds of resonance with ionic forms are expected in this case, depending on the metal attached to the CN group:

$$\underset{\text{I}}{M—C\equiv N} \leftrightarrow \underset{\text{II}}{M^+C^-\equiv N} \leftrightarrow \underset{\text{III}}{M^+C=N^-} \qquad (2)$$

$$\underset{\text{I}}{M—C\equiv N} \leftrightarrow \underset{\text{II}}{M^+=C=N^-} \qquad (3)$$

PAULING[6] has suggested the use of these resonances in the case of complex cyanides in an attempt to remove the negative charge accumulated on the central atom.

Resonance (2) is to be expected when there is a large difference in electronegativity between M and the carbon atom. In this resonance, form III contributes more than form II, since the negative charge is located on the more electronegative nitrogen atom.

Resonance (3) is expected if the difference in electronegativity is not large and M has available *d* electrons for π-bonding. The contribution of the C—N structure from

[5] J. W. LINNETT *Quart. Rev.* **1**, 85 (1947).
[6] L. PAULING *Proc. roy. Soc.* **156**, 254 (1936).

resonance (3) depends on a more complex factor, namely the tendency of the metal atom to donate its unshared *d*-electrons to the carbon atom. This in turn is determined by the following factors:

(1) The tendency of M to be positive, negative or neutral as determined by a scale of electronegativities.

(2) The amount of negative charge accumulated on M from form I, as determined by the oxidation number of M, the per cent ionic characterof the M—C bond and in complex compounds, the co-ordination number of the M ion.

(3) The number of electrons and orbitals available for π-bonding, deduced from the configuration and type of hybridization of the σ-bonds. These have been tabulated by KIMBALL[7] for compounds in which the central atom has a co-ordination number from 2 to 8.

Both types of resonance might be found if the difference in electronegativity is significant and there are available *d*-electrons and orbitals for π-bonding.

In Table 2 the CN frequency of some simple and complex cyanides is listed. These compounds were chosen to exemplify the effect of the different factors considered above.

(a) *Simple cyanides.* In the alkali metal cyanides, *d*-electrons are not available. Therefore resonance (2) is to be expected. Comparison of the two cyanides of group A in Table 1 strongly indicates that the greater the difference in the electronegativities of M and C, the greater is the contribution of the ionic form (III) with a subsequent decrease of the CN frequency.

Group B yields an interesting result. The members of this group have available *d*-electrons; consequently resonance (3) is to be expected along with resonance (2). This is shown to be true from the observed shortening of the M—C distance in

TABLE 2.—THE CN FREQUENCY IN SOME INORGANIC CYANIDES

	Compound	$\bar{\nu}C{\equiv}N$ (cm^{-1})	χ_M[a][6]		Compound	$\bar{\nu}C{\equiv}N$ (cm^{-1})	χ_M[a][8]
1. Simple cyanides				2. Complex cyanides			
A	NaCN	2085[9]	0·9	D	$K_2Pt(CN)_4{\cdot}3H_2O$	2150[11]	2·1[10]
	KCN	2076[9]	0·8		$K_2Pd(CN)_4{\cdot}H_2O$	2143	2·0[10]
B	CuCN	2160	2·2		$K_2Ni(CN)_4{\cdot}H_2O$	2128	1·7[10]
	AgCN	2138	1·9	E	$K_4Ni(CN_4)$	1985	1·7[10]
	AuCN	2217	3·1	F	$KCu(CN)_2$	2110[b][12]	2·2
C	$Pd(CN)_2$	2220	2·0[10]		$K_2Cu(CN)_4$	2094[b][12]	
	$Ni(CN)_2$	2176	1·7[10]				

[a] χ_M represents the electronegativity of the metal.[8]

[b] These are Raman shifts.[12] All the frequencies—except 2150, 2110 and 2094—are obtained from the spectrum of these compounds in nujol. All except 2085, 2075, 2150, 2110 and 2094 are obtained on our spectrophotometer.

[7] G. KIMBALL *J. chem. Phys.* **8**, 188 (1940).
[8] W. GORDY *Phys. Rev.* **99**, 606 (1946).
[9] F. A. MILLER and C. H. WILKINS *Analyt. Chem.* **24**, 1255 (1952).
[10] M. HAISSINSKY *J. chem. Phys.* **46**, 298 (1949).
[11] M. SWEEMY, I. N. MIZUSHIMA and J. V. QUAGLIANO *J. Amer. chem. Soc.* **78**, 889 (1956). They used KBr disk technique.
[12] J. H. HIBBEN *Chem. Rev.* **13**, 454 (1933).

Ag(CN) as determined from X-ray data.[13] For this group, the three factors affecting the contribution of the ionic form in resonance (3) depend only on the electronegativity of M, since the valency state of M, its co-ordination number, and the number of available *d*-electrons are the same for all three metals of this group. Therefore the contribution of the ionic C≡N form and, consequently, the CN frequency

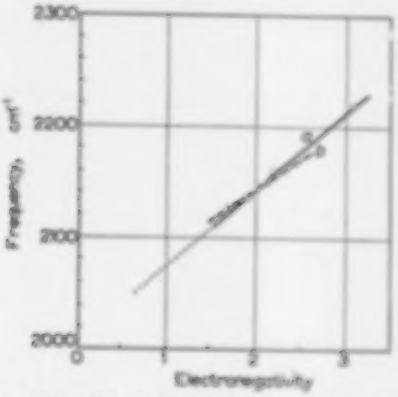

FIG. 1.—The linear relationship between the electronegativity and the CN frequency of cyanides of metals in the same group:
(a) For CuCN, AgCN and AuCN, the GORDY scale of electronegativity is used. The broken line is an extrapolation (see simple cyanides)
(b) For $[Ni(CN)_4]^{-2}$, $[Pd(CN)_4]^{-2}$ and $[Pt(CN)_4]^{-2}$, here the HAISSINSKY scale of electronegativity is used because the values for these metals were not available from GORDY's data.

should depend only on the electronegativity of M. This prediction is found to be true from the straight-line relationship between the CN frequency and the electronegativity of M. This is shown in Fig. 1(a). From this plot, the CN frequency corresponding to an electronegativity value of 0·8 (the electronegativity of potassium) is found to be 2060 cm^{-1}. This value is ~16 cm^{-1} lower than the CN frequency of KCN (2076 cm^{-1}). This lowering is due to the contribution of resonance (3), which does not contribute to the actual state of KCN. This amount of lowering of the CN frequency is found to be about the same as that due to resonance in conjugated organic nitriles. The dependence of the CN frequency on the electronegativity value of the central atom, M, is also shown by comparing the members of group C.

(b) *Complex cyanides.* To see the effect of the three factors mentioned previously, we are going to fix two while discussing the observed frequencies in terms of the third one.

The effect of the first factor is shown by comparing the frequencies of group D of Table 2. Due to the difference in the electronegativities, the contribution of the double-bonded structure should be greater in the case of the nickel complex. This explains its lowered frequency. The straight-line dependence of the CN frequency on the electronegativity for these complexes is shown in Fig. 1(b).

The amount of negative charge accumulated on the central ion (the second factor) depends on the co-ordination number and oxidation number of the central atom, as well as the ionic character of the M—C bond. Generally, high oxidation numbers, low co-ordination numbers of M and/or a high per cent ionic character of the M—C

[13] C. D. WEST *Z. Krist.* **90**, 555 (1935).

bond decrease the amount of negative charge accumulated on the central atom and consequently decrease the contribution of the C=N form. This results in increasing the CN frequency.

The co-ordination number effect is shown by comparing the CN frequencies of the corresponding members of group C and D, and also the compounds of group F.

The effect of the oxidation number is qualitatively shown by comparing the CN frequency of $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_4]^{-4}$. A quantitative discussion for these two complexes has recently been given.[14] The same effect is shown by comparing the CN frequencies of the metal ferro- and ferri-cyanides. The first group absorbs within the range[15] 2040–2090 cm^{-1}, whereas the second group absorbs within the range 2116–2190 cm^{-1}.

The effect of the oxidation number, the percent ionic character and π-bond formation can be shown from the following observations. The replacement of a CN group by NH_3 or H_2O in a ferro- or ferri-cyanide complex does not affect the position of the CN frequency. On the other hand, the replacement of the CN group by NO in sodium ferrocyanide to give sodium nitroprusside, shifts the CN frequency[16] from 2000 cm^{-1} to 2152 cm^{-1}. To explain this observation, one must consider the number of available positions for formation of the three strong π-bonds,[17] which arise from a d^2sp^3 octahedral σ-bonds configuration around the iron atom, as well as the per cent ionic character of these σ-bonds. In the $[Fe^{II}(CN)_5X]^{-n}$ complexes, there are six available positions when X = CN or NO whereas there are only five positions available when X = NH_3 or H_2O. Then the CN bond-order of the double-bonded structure of the first group—in which the three double bonds resonate among six positions—will be greater than that of the corresponding structures in the second group, in which the three double bonds resonate among only five positions. The position of the CN absorption in these complexes relative to that of the hexacyano complex depends upon the contribution of these forms in each complex, which in turn depends on the electronegativity of the replacing group as compared to the CN. In the complexes where X = NH_3 or H_2O, the contribution of the double-bonded ionic form will be less than in $[Fe(CN)_6]^{-4}$. This will compensate for the difference in the CN bond order and gives rise to absorption within the same region. In the case where X = NO, the per cent ionic character of the Fe—N bond allows resonance with the double-bonded ionic form to such an extent that the iron resembles Fe^{+3} or even Fe^{+4}.[15] Therefore a much smaller contribution of the double-bonded structure would be needed in this case to attain electrical neutrality than in $[Fe(CN)_6]^{-4}$ and even less than in the case of $[Fe(CN)_6]^{-3}$. This explains the higher CN frequency of sodium nitroprusside (2152 cm^{-1}) as compared to sodium ferricyanide (2115 cm^{-1}).

EXPERIMENTAL

(a) *Preparation of the samples.* According to BARBER,[17] CuCN was made from copper sulphate, potassium cyanide, and sodium bisulphate at 60°C. AgCN was prepared from KCN and $AgNO_3$. AuCN was prepared by the action of prussic acid on auric hydroxide. $Pd(CN)_2$ and $Ni(CN)_2$ were prepared by the action of KCN on a corresponding water-soluble salt. $K_2[Pd(CN)_4]\cdot H_2O$ and $K_4[Ni(CN)_4]\cdot H_2O$ were prepared by dissolving the corresponding $M(CN)_2$ in an excess of KCN and evaporating to get the complex salt. $K_4[Ni(CN)_4]$ was made by the reduction of a small amount

[14] M. F. A. EL-SAYED and R. K. SHELINE Accepted for publication in the *J. Amer. chem. Soc.*
[15] G. EMSCHIULLER *C. R. Acad. Sci., Paris* **238,** 1414 (1954).
[16] E. F. G. HERINGTON and W. KYNASTON *J. chem. Soc.* 3555 (1955).
[17] H. J. BARBER *J. chem. Soc.* 79 (1943).

of $K_4[Ni(CN)_4]\cdot H_2O$ with metallic potassium in liquid NH_3.[18] Ammonia was eliminated by gentle suction after evaporation at room temperature, followed by the passage of oxygen-free nitrogen through the system.

(b) *Infra-red spectrum.* The spectra of all these compounds were taken on a Perkin–Elmer model 21 spectrophotometer, using the mull technique in nujol. The spectrophotometer was calibrated by obtaining the spectrum of water-vapour in the air and checking the peaks recorded against standard values. A curve was then drawn which correlates the frequency corrections and the observed frequencies of the water-vapour. From this curve and the observed frequencies of the compounds the corresponding corrections were calculated and applied.

[18] J. E. Eastes and M. Wayland *J. Amer. chem. Soc.* **64**, 1187 (1942).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 194 to 198. Pergamon Press Ltd., London

THE FLUORIDES OF URANIUM—I

LIQUID–VAPOUR EQUILIBRIA IN THE SYSTEMS URANIUM HEXAFLUORIDE—CHLORINE TRIFLUORIDE AND URANIUM HEXAFLUORIDE—BROMINE PENTAFLUORIDE

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Abstract—The system uranium hexafluoride–chlorine trifluoride exhibits complete miscibility in the liquid phase at 67°C but partial miscibility at 75°C over a limited composition range. No azeotropes exist in this system.

The system uranium hexafluoride–bromine pentafluoride exhibits complete miscibility over the range 68–80°C and has a single maximum vapour pressure azeotrope at a composition corresponding to a mole fraction of 0·1 of uranium hexafluoride, approximately.

The work was done to determine the conditions necessary for purifying uranium hexafluoride from various fluoride impurities by distillation. Jarry *et al.*[1] have described liquid–vapour equilibria in the system uranium hexafluoride–hydrogen fluoride, and Rogers *et al.*[2] refer to the existence of a maximum vapour pressure azeotrope mixture in the system chlorine trifluoride–hydrogen fluoride. The systems now discussed were studied to give further background information before attempting fractional distillation of fluoride mixtures.

EXPERIMENTAL

Chemicals

Uranium hexafluoride, chlorine trifluoride and bromine pentafluoride were all purified by redistillation, and the halogen fluorides were shown to have purities greater than 99 per cent by chemical analysis.

Apparatus

A line diagram of the apparatus is shown in Fig. 1. *A* was a heavy-walled Monel pressure vessel, of capacity 0·5 l., approximately, fitted with a dip pipe for liquid sampling. The dip pipe was of $\frac{1}{2}$ in. nominal bore copper tubing flared to $\frac{1}{2}$ in. at the open end and fitting to within $\frac{1}{2}$ in. of the base of the vessel. Control valves allowed for inward feed and for liquid and vapour sampling. The vessel was also fitted with a diaphragm pressure gauge G_1 (0–200 p.s.i.g., Budenberg Gauge Co., Altrincham, Cheshire) which was precalibrated against a standard test gauge using nitrogen. The vessel was mounted in a horizontal rocking device and was connected to the rest of the apparatus by means of a $\frac{1}{4}$ in. nominal bore copper spiral which allowed lateral shaking. The copper spiral led to a manifold with connexions to a waste gas buffer vessel *B* (1 l.) used to enable purging of all sampling lines at rig ambient temperature, a sonic analyser and trapping system, and a large gas holder *D* (50 l.) and secondary trapping system.

[1] R. L. Jarry, F. D. Rosen, C. F. Hale and W. Davis, Jr. *J. phys. Chem.* **57**, 905 (1953).
[2] M. T. Rogers, J. L. Speirs and M. B. Panish U.S. Atomic Energy Commission Report AECU 3097 (1955).

All valves which were to be in extensive contact with corrosive gases were ¼ in. nominal bore chlorine valves (Paterson Eng. Co. Ltd., London). For normal vacuum work ¼ in. nominal bore process gas valves (Weir Eng. Co. Ltd., Glasgow, to U.K.A.E.A. specification) were used. Flanged joints with fully trapped neoprene rings were used as demountable vacuum connexions.

The sonic analyser assembly consisted of a buffer vessel *C* to which the sonic tube was attached; beyond the sonic tube a ¼ in. nominal bore copper pipe led to a hard-soldered-capsule absolute pressure gauge G_3 (0–800 mm mercury absolute, Kelvin and Hughes Ltd., Glasgow). The sonic analyser was of the type described by PULSFORD,[3] and its application to binary gas mixtures has been described

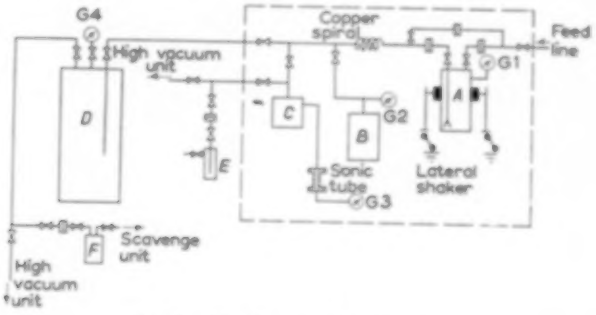

FIG. 1.—Line diagram of apparatus

elsewhere;[4] its calibration on theoretical grounds is described by PULSFORD.[3] The validity of the sonic analyser calibration was checked for a particular mixture of uranium hexafluoride and chlorine trifluoride by chemical analysis of a potassium hydroxide hydrolysate of the mixture. From chemical analysis a value of 0·303 was obtained for the mole fraction of uranium hexafluoride in the test mixture, compared with the value of 0·298 obtained by using the sonic analyser. These results agree within the limits of experimental error.

The pressure vessel and analyser system were mounted in an air thermostat, pressure gauge G_1 being read through an inspection window. G_2 and G_3 fitted into the walls of the air thermostat. The ambient temperature of the chamber, and temperatures of vessels *A* and *C* and the sonic tube, were recorded by means of a Multelec recorder (George Kent, Ltd., Luton, Bedfordshire) and in all cases agreed to ± 1°C. Valves within the air thermostat could be controlled from outside by means of extension spindles.

Experimental procedure for system uranium hexafluoride–chlorine trifluoride

After vacuum testing of the whole apparatus (permitted standard 30 μ of mercury per hour inleakage at 10 μ of mercury pressure) and pressure testing of the vessel *A* (test pressure 200 p.s.i.g. nitrogen), the equipment inside the air thermostat was stabilized against corrosion by treatment with chlorine trifluoride gas (350 mm pressure) for 24 hr at 85°C. Ancillary equipment was treated with gaseous chlorine trifluoride at room temperature for 24 hr. This was removed from the system by pumping through calcium chloride towers (in which the chlorine trifluoride is converted to chlorine) with a rotary pump filled with chlorofluorolube (Imperial Chemical Industries, Ltd., Widnes) and venting the chlorine to atmosphere. After the equipment had been purged with dry nitrogen it was again pumped down to high vacuum.

A known mixture of uranium hexafluoride and chlorine trifluoride was introduced into *A* by distillation from weighed sealed vessels whilst *A* was cooled in liquid nitrogen. The pressure vessel was then isolated. Coolant was removed from around *A* and the thermostat chamber was closed and heated to the required temperature. After this temperature had been reached, the shaking device was started: *A* was then shaken for 1 hr, and then allowed to settle for 15 min to permit possible separation into two liquid layers. The pressure on G_1 was then recorded, and the liquid and vapour phases were sampled separately through the appropriate sample valves and analysed by the sonic analyser.

[3] E. W. PULSFORD *J. Brit. Instn. Radio Engrs.* **15**, 117–128 (1955).
[4] U.K.A.E.A. (Collected Authors). *The Sonic Analyser*. Issued at the Physical Society Exhibition (1955).

The gas holder *D* was used to retain material purged from the sample lines. Weighed vessels *E* and *F* were used to receive condensed samples for occasional chemical analytical checks. All the system except the vessel *A* was then completely evacuated, the rig cooled down and the gross composition of

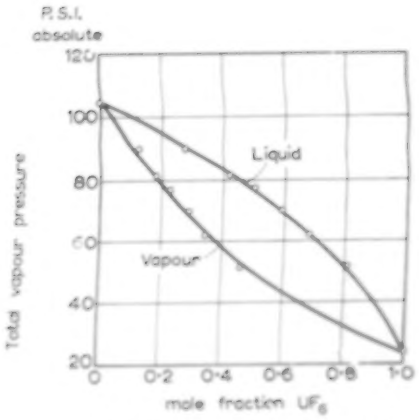

FIG. 2.—System UF_6–ClF_3 at 67° C

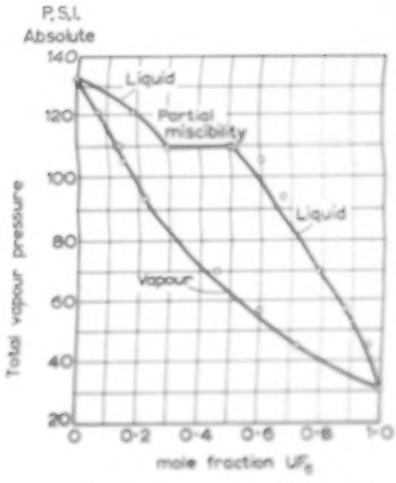

FIG. 3.—System UF_6–ClF_3 at 75° C

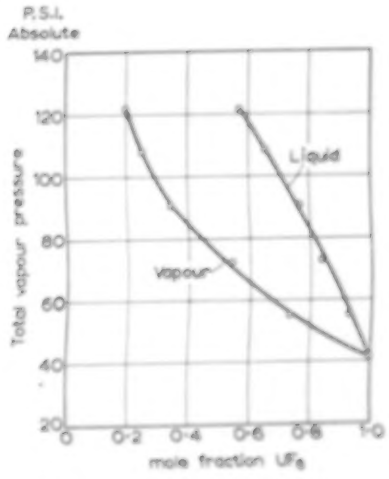

FIG. 4.—System UF_6–ClF_3 at 84° C

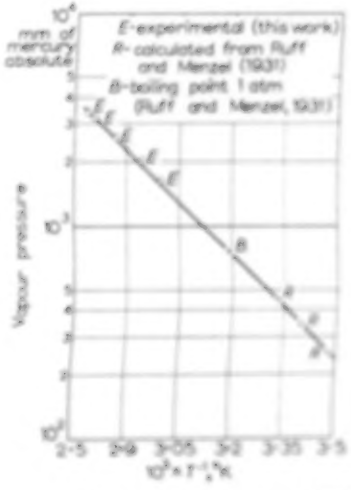

FIG. 5.—Vapour pressure of BrF_3

the mixture in A was adjusted to the next required value. The experiment as a whole was then repeated.

Experiments were carried out at 67° and 75° C for the whole range of compositions from pure uranium hexafluoride to pure chlorine trifluoride, and at 84° C for liquids containing 1·0–0·565 mole fractions of uranium hexafluoride. Higher concentrations of chlorine trifluoride in the latter case would have given rise to pressures greater than the allowable safety margin, and therefore the rest of the system was not studied. The pressure gauge was checked at the end of each series of experiments and was found to have operated without drift.

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Values for the vapour pressure of pure uranium hexafluoride were taken from Weinstock and Cunn;[3] and the vapour pressure of pure chlorine trifluoride was extrapolated from the supplier's data sheet.[4] Results are depicted graphically in Figs 2–4.

Experimental procedure for system uranium hexafluoride–bromine pentafluoride

This was identical with that used in the previous system except that, in liquid sampling, any material entrapped in the dip line at the start of sampling was purged into the vessel *B* and isolated there until the sonic analyser reading had been taken. In a preliminary experiment, the vapour pressure curve of bromine pentafluoride above 1 atm was determined by maintaining 50 g in the pressure vessel *A* at various temperatures for 1 hr and observing the pressure in each case. Results are shown in Figs. 5 and 6.

DISCUSSION

System uranium hexafluoride–chlorine trifluoride

The phase diagrams for liquid–vapour equilibria in this system show that no azeotropic mixture exists. At 67°C the components are completely miscible, but at

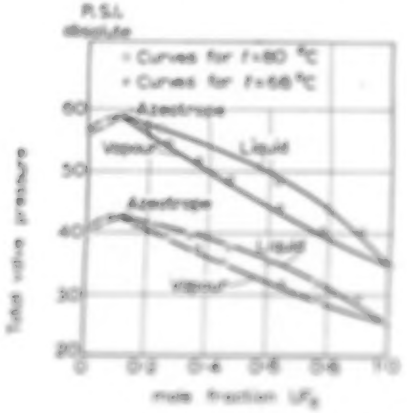

FIG. 6.—System UF_6–BrF_5 at 68 and 80°C

75°C a partial miscibility region appears between the limits of 0·3–0·5 mole fractions of uranium hexafluoride (see Figs. 2 and 3). This points to the existence of a lower critical solution temperature between 67 and 75°C. Experiments at 84°C had to be suspended, as the pressure test safety factor of the equipment would have been exceeded at high chlorine trifluoride concentrations. The absence of an azeotrope means that these two components would be separable by fractional distillation.

System uranium hexafluoride–bromine pentafluoride

The determined vapour pressures of bromine pentafluoride above 1 atmosphere fall upon the extrapolation of the curve given by Ruff and Menzel[5] for pressures below 1 atm, as shown in Fig. 5.

In the two-component system, the phase diagrams show complete miscibility at the

[3] J. Weinstock and R. Cunn *J. chem. Phys.* **16**, 436 (1948).
[4] *Data sheet for chlorine trifluoride*. Imperial Chemical Industries, Ltd., Cunard Building, Liverpool (1952).
[5] O. Ruff and W. Menzel *Z. anorg. chem.* **202**, 49 (1931).

temperatures studied, and also the existence of an azeotrope of maximum total vapour pressure, and composition 0·1 mole fraction of uranium hexafluoride.

It is therefore not possible to separate these components by direct fractional distillation.

Acknowledgements—The authors are indebted to Mr. E. DUNCOMBE for modifications and improvements to the design of the Pulsford-type sonic analyser, to Messrs. J. T. JOHNSTON and J. LEECE for assembly of the sonic analyser unit, and to the Managing Director of the Industrial Group, United Kingdom Atomic Energy Authority, for permission to publish this work.

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THE FLUORIDES OF URANIUM—II

DISTILLATION OF MIXTURES OF CORROSIVE VOLATILE FLUORIDES INCLUDING URANIUM HEXAFLUORIDE

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Abstract—Distillation of binary systems has shown that uranium hexafluoride is completely separable from chlorine trifluoride and bromine trifluoride, but forms azeotropes with hydrogen fluoride and bromine pentafluoride. At pressures above atmospheric, uranium hexafluoride and bromine interdistil without separation. Hydrogen fluoride forms azeotropes with bromine, bromine trifluoride, bromine pentafluoride and chlorine trifluoride. A distillation method has been evolved for purifying uranium hexafluoride from a ternary mixture with chlorine trifluoride and hydrogen fluoride.

CORROSIVE chemical handling techniques, some of which have been referred to in Part I,[1] were extended to cover the attempted separation, by fractional distillation, of various systems containing some halogens, halogen fluorides, hydrogen fluoride and uranium hexafluoride.

EXPERIMENTAL

Apparatus

A line diagram of the apparatus is given in Fig. 1. The boiler had a capacity of 2·5 l., and was constructed of mild steel, nickel-plated on the inside. The fractionating column consisted of a 5 ft length of 1 in. nominal bore Monel tubing packed with $\frac{1}{8}$ in. Dixon ring packing fabricated from nickel gauze. A cold thimble-type condenser, also in Monel, was mounted above the column. The unions between boiler and column, and column and condenser, were spigoted and grooved flanges with fully-trapped aluminium sealing rings. A series of sample points along the column led to a manifold and sonic analyser system (cf. Part I[1]). A dip pipe from the boiler led into the analyser system and enabled liquid samples to be examined. Pressure gauges P_1 and P_2 (diaphragm type, 0–200 p.s.i.g.; Budenberg Gauge Co., Altrincham, Cheshire) were fitted at the base and top of the column. P_2 had incorporated a safety device which cut off the boiler heater at a preset pressure. In the sonic analyser system, 0–800 mm mercury absolute pressure gauges P_3 and P_4 (Kelvin and Hughes Ltd., Glasgow) were used. All valves in contact with corrosive gases were $\frac{1}{4}$ in. nominal bore chlorine valves (Paterson Eng. Co., London).

Provision was made for inward feed of test substances, for scavenging to dry calcium chloride or wet scrubbers, and for vacuum and pressure testing. That part of the system above the broken line in Fig. 1 was enclosed in a brick cubicle which could be evenly heated to temperatures up to 100 ± 4°C. Lines to the pressure gauges were heat-traced in order to prevent condensation of liquid under high pressure. Valve operations were controlled by extension spindles passing through the brick wall between rig and control cubicles. Pressure gauges were read through an inspection window of $\frac{1}{4}$ in. shatterproof glass backed by $\frac{1}{4}$ in. Perspex sheet.

The boiler, column and condenser were enclosed by aluminium casing packed with a 5 in. radial thickness of "Santocel" lagging powder (Monsanto Chemical Co., U.S.A.). The boiler lagging was in a detachable box to allow cooling of the boiler during still-charging. The boiler was heated with a plate heater (maximum energy input 850 W) which was controlled from a variable-voltage transformer fed with a stabilized 230 V a.c. input. The sonic tube was housed in an insulated box to damp out the variations in cubicle ambient temperature. The condenser was fed through a Rotameter with water from a thermostatically-controlled bath sited in the control cubicle.

[1] J. F. ELLIS and K. D. B. JOHNSON *J. inorg. nucl. Chem.* **6**, 194 (1958).

Thermocouples were placed to allow observation of boiler temperatures (using a thermowell) and water temperatures at the points of entry to and exit from the condenser. Temperatures along the column and of the sonic tube could also be measured. All thermocouple points are shown in Fig. 1, those along the column being equidistant. Temperatures of the boiler, column head and sonic tube were recorded on a Multelec recorder (George Kent, Ltd., Luton, Beds.) and the rest could be observed by preselection on a multipoint instrument (Cambridge Instrument Co.).

Before installation, the boiler column and condenser assembly was hydraulically tested to 500 p.s.i.g.

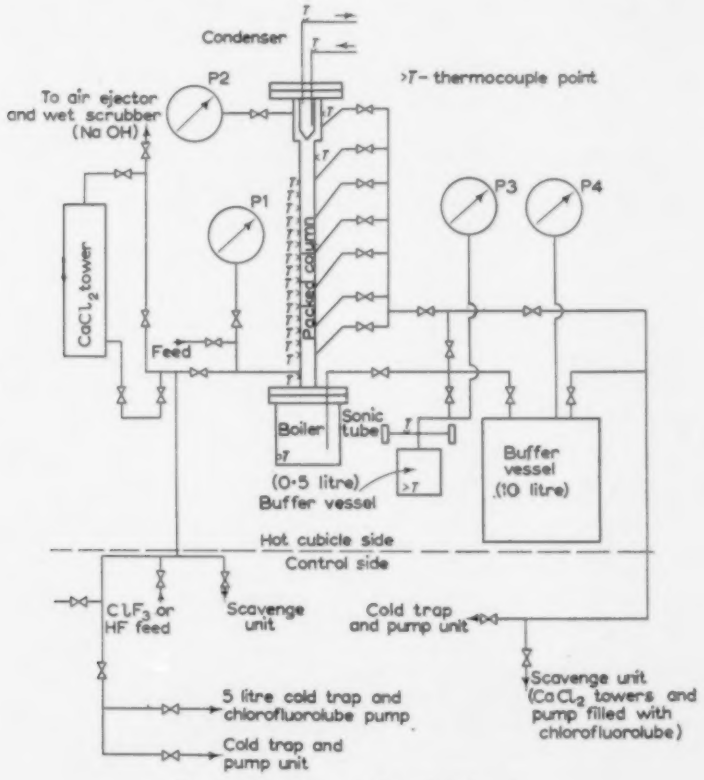

FIG. 1.—Line diagram of fractionation rig.

Determination of column efficiency

The standard efficiency of this column under total reflux at 1 atm pressure was determined for low boil-up rates using a mixture of ethylene dichloride and benzene (after WARD[2]). At a boil-up rate of 525 g/hr the still pot and vapour samples contained 0·137 and 0·875 mole fraction of benzene, respectively. The FENSKE equation[3] gave a value of 36 theoretical plates for the column under these conditions.

RESULTS

System uranium hexafluoride–chlorine trifluoride

The system was vacuum-tested to a standard of 36 μ/hr in leakage at 10 μ pressure, and the boiler, column and condenser assembly was pressure-tested after final installation to 180 p.s.i.g. with nitrogen. The whole system was then stabilized against

[2] C. C. WARD U.S. Bur. Mines, Tech. Paper No. 600 (1939).
[3] S. FENSKE *Industr. engng. Chem.* (*Industr.*) **24**, 82 (1932).

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corrosion by treatment with chlorine trifluoride (500 mm pressure) at 100°C. During operation, the cycle of vacuum test, pressure test and fluorination was completed as a matter of routine every second run. Chlorine trifluoride was withdrawn by a scavenge unit as described in Part I.[1]

For investigation of the uranium hexafluoride–chlorine trifluoride system the boiler was charged with 2·1 kg of the former and 25 g of the latter. Water flow

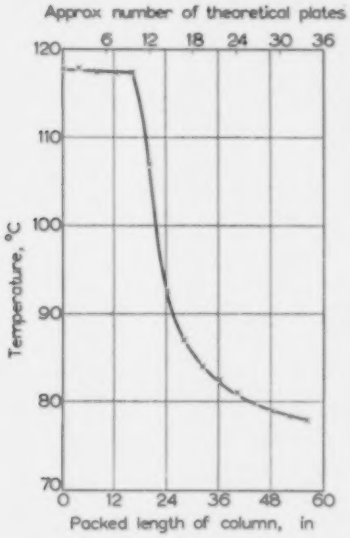

FIG. 2.—ClF_3–UF_6 system: temperature distribution along column at start of sampling.

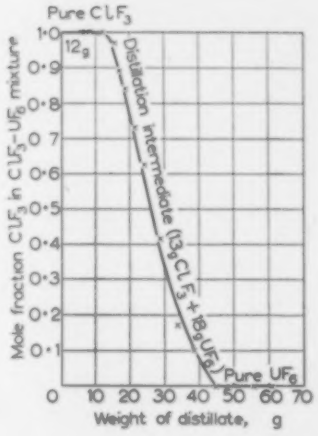

FIG. 3.—Distillation of UF_6–ClF_3 mixture.

through the condenser was fixed at 20 l./h at 70°C, and the hot cubicle ambient temperature was set at 75°C. After preflooding by turning on full boiler power for a short time, the system was brought to equilibrium over 24 hr at a boiler power input of 150 W. At this stage there was a sharp break of 30°C in the temperature along the column (see Fig. 2), indicating the separation of the two components over approximately 5–7 theoretical plates. A sample from the boiler showed that it contained pure uranium hexafluoride. A vapour sample was taken from the topmost sample point and analysed by a sonic analyser, as described in Part I.[1] The weight of each sample was calculated from the pressure in the known volume of the analyser system. The operating pressure at the start of sampling was 80 p.s.i.g. The first samples were of pure chlorine trifluoride; this was followed by a distillation intermediate, viz. a mixture of chlorine trifluoride and uranium hexafluoride, with the chlorine trifluoride content continually diminishing as sampling proceeded. Finally pure uranium hexafluoride was obtained from the vapour sampling point. The results of the distillation are set out in Fig. 3, and show the separation to be satisfactory. The operational wastage of uranium hexafluoride was only 18 g; this is a characteristic of the column and does not depend on the total charge per batch.

The experiments confirm the observation in Part I that the two components of the system should be separable by fractional distillation.

System uranium hexafluoride–hydrogen fluoride

Liquid–vapour equilibria in this system have been investigated by JARRY *et al.*[4] The system exhibits limited miscibility in the liquid phase up to the consolute point (101°C), and the shape of the isothermal equilibrium curve below 101°C is of Type I of the general types of partial miscibility system outlined by MARSHALL.[5] Thus distillation below the consolute point should give rise to a constant-boiling mixture as a result of the partial miscibility, whilst above it a true azeotrope should be formed. These predictions are confirmed by experiment.

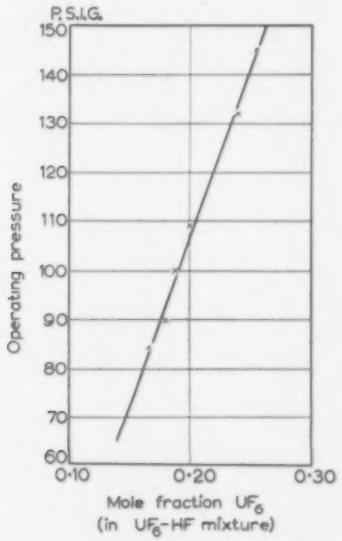

FIG. 4.—Distillation of UF_6–HF mixture: variation in azeotrope composition with operating pressure.

The boiler was charged with 2·11 kg of uranium hexafluoride and 20 g of anhydrous hydrogen fluoride. The water flow through the condenser and the cubicle ambient temperature were set as for the preceding system, and the run was brought to equilibrium in the same way. At this time a break of 44° in the temperatures along the column occurred over a distance of about 5 theoretical plates, showing the separation between uranium hexafluoride and light fraction. A boiler sample showed that the boiler contained only uranium hexafluoride. A vapour sample, taken through the topmost sampling point under operating pressure of 90 p.s.i.g., contained a mole fraction of 0·18 of uranium hexafluoride; a duplicate sample confirmed this. By adjusting input heat to the boiler and heat withdrawal from the condenser, the operating pressure was varied between 84 and 145 p.s.i.g. whilst a series of samples were taken. The results of plotting operating pressure against still-head composition are shown in Fig. 4. Over the range covered, the mole fraction of uranium hexafluoride in the still-head mixture rises linearly with the operating pressure.

[4] R. L. JARRY, F. D. ROSEN, C. F. HALE and W. DAVIS, JR. *J. phys. Chem.* **57**, 905 (1953).
[5] J. MARSHALL *J. chem. Soc.* **89**, 1350 (1906).

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The system chlorine trifluoride–hydrogen fluoride

ROGERS *et al.*[6] mention the occurrence of an azeotrope with maximum vapour pressure in this system.

The boiler was charged with 0·45 kg of chlorine trifluoride and 14 g of anhydrous hydrogen fluoride. Water flow through the condenser was fixed at 30 l/hr at 65°C, and the cubicle ambient temperature was controlled at 55°C. The system was allowed to come to equilibrium over 24 hr with a heat input of 54 W to the boiler. All the column thermocouples were then at 63 ± 2°C and the operating pressure was 88 p.s.i.g. Two samples then taken through the topmost sample point were identical, consisting

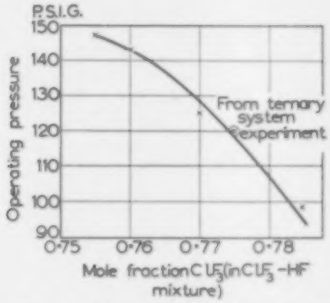

FIG. 5.—Distillation of HF–ClF_3 mixture: variation in azeotrope composition with operating pressure.

of a mixture containing a mole fraction of 0·785 chlorine trifluoride. The variations of still-head composition with operating pressure were investigated as in the previous system. The results, plotted in Fig. 5, show that increase in operating pressure caused diminution of the amount of chlorine trifluoride in the azeotrope; the relationship did not appear to be linear.

Distillation of the ternary mixture uranium hexafluoride, chlorine trifluoride and hydrogen fluoride

For this investigation the boiler was charged with uranium hexafluoride (2·46 kg), chlorine trifluoride (185 g) and anhydrous hydrogen fluoride (4 g). Water flow through the condenser was set at 15 l/hr at 70°C, and the rig cubicle ambient temperature was set at 75°C. After attempted preflooding, the system was allowed to come to equilibrium over 24 hours with a heat input of 74 W to the boiler. At this time the operating pressure was 120 p.s.i.g. A break of 36°C in the temperatures along the column occurred over a distance of approximately 8–10 theoretical plates, indicating separation of uranium hexafluoride from light fraction. A liquid sample showed that the boiler contained pure uranium hexafluoride. A series of vapour samples was found to be uranium-free by chemical tests. The sonic analyser result gave the composition as a mixture of chlorine trifluoride (mole fraction 0·775) and hydrogen fluoride. This figure, at 120 p.s.i.g. working pressure, lies well on the curve of Fig. 5, which shows variation of the composition of the chlorine trifluoride–hydrogen fluoride azeotrope with pressure. Samples of this azeotrope were taken off until

[6] M. T. ROGERS, J. L. SPEIRS and M. B. PANISH U.S. Atomic Energy Commission Report AECU 3097 (1955).

almost all the hydrogen fluoride had been removed. The chlorine trifluoride content of the samples then increased until pure chlorine trifluoride was obtained from the vapour sampling point. All the intermediate samples were shown to be uranium-free by chemical tests. The system was then resolved into distillation of a mixture of uranium hexafluoride and chlorine trifluoride, and this was readily accomplished as described previously. Fig. 6 shows the result of distillation of hydrogen fluoride and chlorine trifluoride above uranium hexafluoride up to the appearance of pure chlorine trifluoride in the samples from the vapour take-off point. The uranium

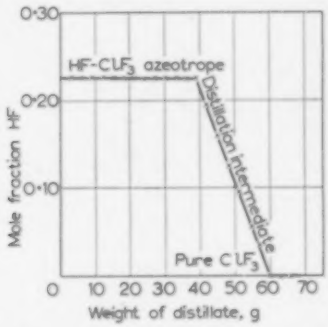

Fig. 6.—Distillation of HF and ClF_3 over UF_6.

hexafluoride–hydrogen fluoride azeotrope can thus be broken by adding sufficient chlorine trifluoride to remove all hydrogen fluoride on distillation as the hydrogen fluoride–chlorine trifluoride azeotrope.

The system uranium hexafluoride–bromine

There have been no publications concerning liquid–vapour equilibria in this system. As the boiling point of bromine at 1 atm is 58·5°C and the sublimation point of uranium hexafluoride at the same pressure is 56·5°C, it was thought that separation with this fractionation unit would be most difficult.

It was found to be impossible to effect any separation. Two mixtures were distilled, one having a mole fraction of 0·44 and the other 0·54 of bromine. In each case the still-head composition was identical with that in the boiler even after maintaining steady conditions for 24 hr. Since no separation occurred in either case, there can be no possibility of formation of a constant-boiling mixture in the system.

The system uranium hexafluoride–bromine trifluoride

The boiler was charged with 0·44 kg of bromine trifluoride, previously purified by redistillation, and 0·37 kg of uranium hexafluoride. Water flow through the condenser was fixed at 20 l/hr at 75°C and the rig cubicle ambient temperature was maintained at 95°C. The system was brought to equilibrium over 1 hr with a heat input of 125 W to the boiler. At this stage the operating pressure was 25 p.s.i.g. A break of 45° in the temperatures along the column occurred over a distance of approximately 5 theoretical plates, indicating separation of the two components. A sample from the boiler then showed that it contained only bromine trifluoride, and a series of samples showed pure uranium hexafluoride at the still-head. Distillate was then removed

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slowly and continuously over a period of several hours. The interface between the two components moved steadily up the column, until finally pure bromine trifluoride was taken off through the topmost sample point.

These two components are thus readily separable by fractional distillation.

System uranium hexafluoride–bromine pentafluoride

Liquid–vapour equilibria in this system are described in Part I.[1] Complete miscibility is found throughout the composition range, and there is a single azeotrope with maximum vapour pressure.

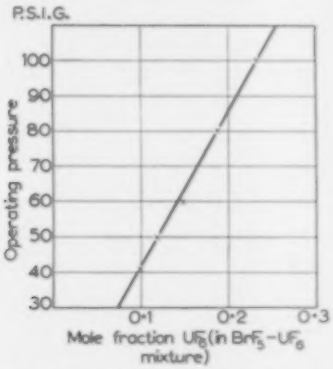

FIG. 7.—Distillation of UF_6–BrF_5 mixture: variation in azeotrope composition with operating pressure.

TABLE I.—COMPOSITIONS OF AZEOTROPES IN SYSTEMS OF HYDROGEN FLUORIDE WITH BROMINE AND BROMINE FLUORIDES

Component I	Component II	Azeotrope composition expressed as mole fraction of component I	Operational pressure range (p.s.i.g.)
Bromine	Hydrogen fluoride	0·14	65–97
Bromine trifluoride	Hydrogen fluoride	0·06	40–58
Bromine pentafluoride	Hydrogen fluoride	0·30	42–45

The boiler was charged with 2·30 kg of uranium hexafluoride and 90 g of bromine pentafluoride. Water flow and cubicle ambient temperature were fixed as for the system chlorine trifluoride–uranium hexafluoride. The equipment was allowed an equilibrium period of one hour with a power input of 150 W to the boiler. At this stage there was 10° variation in the temperature along the column from base to head, but no sharp break at any one point. The operating pressure was 41 p.s.i.g. Three vapour samples then taken were all identical, containing a mole fraction of 0·1 of uranium hexafluoride. The variation of still-head composition with pressure was then studied as in the uranium hexafluoride–hydrogen fluoride system. The results,

given in Fig. 7, show a linear variation with the uranium hexafluoride content rising with increased operating pressure.

Systems involving hydrogen fluoride as one component with bromine, bromine trifluoride and bromine pentafluoride

There are no published data on liquid–vapour equilibria in any of these binary systems. Investigations with the fractionation unit show that an azeotrope exists in each case. The compositions of these azeotropes are shown in the Table 1.

No significant variation of azeotrope composition with operating pressure was observed in any of these systems.

Acknowledgements—Considerable assistance was given by the Engineering Section of the Laboratories, notably by Mr. W. Law with design of the rig and Mr. R. Halliwell with its construction. This paper is published with the permission of the Managing Director of the Industrial Group, United Kingdom Atomic Energy Authority.

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J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 207 to 209. Pergamon Press Ltd., London

PREPARATION OF THE NIOBIUM (IV) AND NIOBIUM (III) IODIDES*

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(*Received* 10 *October* 1957)

Abstract—Conditions are reported for (1) the preparation of niobium(V) iodide, (2) the preparation and sublimation of niobium(IV) iodide by thermal decomposition of the pentaiodide and (3) the subsequent disproportionation to niobium(III) iodide. Properties and powder patterns are given for the three iodides.

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ONLY fragmentary evidence is available in the literature on the lower iodides of niobium. KÖRÖSY[1] found that thermal decomposition of NbI_5 at 300–400° in vacuum resulted in the formation of material varying in composition from $NbI_{2.33}$ to $NbI_{2.5}$. No evidence was reported to indicate whether this was a pure phase, although he suggested the compound $NbI_3 \cdot NbI_2$ might be formed. ALEXANDER and FAIRBROTHER[2] also obtained evidence for an unidentified lower iodide. However, in neither investigation was the starting NbI_5 free of excess metal and also, presumably, lower iodides. During an investigation of the preparation and properties of niobium pentaiodide it was observed that thermal decomposition of this material resulted in the formation of a number of lower iodides. The present paper deals with the first two of these, the tetraiodide and the tri-iodide.

RESULTS AND DISCUSSION

Thermal decomposition of niobium (V) iodide results in a number of dissociation and disproportionation reactions. In the majority of cases these reactions were observed by heating NbI_5 to various temperatures while the other end of the evacuated container remained at 30–40°. Thus, evolved iodine produces a pressure of about 0·8 mm throughout the experiments. Loss of iodine from the pentaiodide is first observed at ca. 200°. The simultaneous sublimation of a small amount of NbI_5 also occurs; this process is much more rapid at higher temperatures and iodine pressures. When the decomposition is carried out at 270° the residue obtained is pure, grey NbI_4. The tetraiodide, like the pentaiodide, is extremely sensitive to water and oxygen.[3]† The NbI_4 can be sublimed at 300°; disproportionation also produces small amounts of the more volatile NbI_5.

When this disproportionation is carried out at 430°, the residue is the black NbI_3.

* Contribution No. 555. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

† Preliminary single-crystal X-ray studies of NbI_5 and NbI_4 show the former to be related to $NbCl_5$ although not isomorphous with it. The NbI_4 is orthorhombic, probably space group *A2am*, *Ama2* or *Amam* with $a_0 = 13{\cdot}98$, $b_0 = 13{\cdot}27$ and $c_0 = 7{\cdot}73$ Å.

[1] F. KÖRÖSY *J. Amer. chem. Soc.* **61**, 838 (1939).
[2] K. M. ALEXANDER and F. FAIRBROTHER *J. chem. Soc.* 2472 (1949).
[3] L. DAHL Private communication.

This salt is stable to air for several days at room temperature, being quite similar in inertness to the niobium (III) chloride and bromide.[4]

If the temperature is raised to 450–500° in this preparation, distinct bands of sublimed NbI_3, NbI_4 and NbI_5 are observed toward the cooler end of the furnace. Disproportionation of the tri-iodide occurs in the process, and the residue apparently contains a lower iodide, perhaps NbI_2. Metal is produced by prolonged heating at 540° and quite readily at 800°.

Due to the non-isothermal conditions employed in these studies it is difficult to relate all of the above observations to equilibrium reactions of the various iodides. Quantitative studies of the various dissociation, disproportionation and sublimation equilibria now under way will characterize these systems more fully.

EXPERIMENTAL

Niobium (V) *iodide*. NbI_5 was prepared by the reaction of the metal with a 10–15 per cent excess of iodine. The niobium metal was Fansteel sheet, obtained through the courtesy of Dr. O. N. Carlson of this Laboratory. The halogen (J. T. Baker reagent) was first purified by sublimation *in vacuo* at ca. 80°. The metal and iodine were contained in opposite ends of an evacuated, V-shaped Pyrex tube, and the metal heated to 510° and the iodine to 180°. The reaction was carried to completion in 36–48 hr, during which time the product sublimed to the junction of the two furnaces. Both ends were then cooled uniformly; when the salt was at ca. 70°, the iodine end was immersed in a −80° bath and then sealed off. The NbI_5 obtained was in the form of brass-coloured plates.*

Use of niobium metal powder as a starting material was less satisfactory, as this apparently contained considerable amounts of oxygen. In this case appreciable amounts of a slightly more-volatile material, apparently $NbOI_3$, were found as black needles contaminating the NbI_5.

Niobium (IV) *iodide*. Samples of NbI_5 were transferred in a helium-filled dry box to glass tubes equipped with ball joints for evacuation. Because of the extreme sensitivity of NbI_5 to moisture, the containers were evacuated and flamed before being taken into the box. After being filled, they were re-evacuated and sealed off.

The preparation of NbI_4 was accomplished by heating the NbI_5 to 270° for 48 hr, collecting the evolved iodine in the other end of the tube at about 35° (v.p. of I_2 = ca. 0·8 mm). All subsequent preparations were also made in the presence of such an iodine pressure. The reaction can be carried out more rapidly by first decreasing the particle size of the NbI_5; this was accomplished either by grinding or decomposition at 300°C for 6 hr, followed by recombination at 250°. Sublimed tetraiodide was obtained by raising the decomposition temperature to 300°, giving dark-grey, metallic-appearing crystals in the form of elongated hexagonal plates and fine needles. The salt gives brown and blue solutions in water and dil. HCl, respectively, and is paramagnetic, as expected.

Niobium (III) *iodide*. The salt was prepared in a manner similar to that already described; heating a higher iodide to 425–430° for 48 hr with the other end of the tube at 40°. A sublimate of NbI_3 can be obtained at 450–500°, although analysis indicates a small amount of contamination by other iodides. A lower iodide is

* *Note added in proof:* R. F. ROLSTEN *J. Amer. chem. Soc.* **79**, 5409 (1957) reports preparation of NbI_5 from the elements at 265° to 290°. The procedure does not involve sublimation of the product.

[4] C. H. BRUBAKER and R. C. YOUNG *J. Amer. chem. Soc.* **73**, 4179 (1951).

apparently somewhat volatile at 500°. The NbI_3 is insoluble in water or conc. HCl, and soluble in dil. HNO_3.

Analyses. A sample of the salt was transferred in the dry box to a small weighing bottle and the ground joint lightly greased. After weighing this in air, the salt was poured into a crucible, the bottle quickly recapped, and the weight of the sample determined by difference (corrected for buoyancy). Since only niobium and iodine were present, the analysis was carried out by ignition to Nb_2O_5. Typical I/Nb ratios of 5·02, 4·98, 4·96; 4·07, 4·03, 3·98; 3·04, 3·03, 2·97 were obtained for the three salts.

Powder patterns. Diffraction patterns were obtained on samples contained in 0·1 mm i.d. capillaries that had been filled in the dry box. An 11·46 cm Philips camera was used with Ni-filtered CuK_α radiation; absorption corrections were not applied. The following spacings, in ångströms, with relative intensities indicated in parentheses, were the principal ones observed for the three iodides:

NbI_5: 8·0(5), 3·21(9), 3·04(10), 2·38(5), 2·34(5), 1·999(6), 1·852(5), 1·823(6), 1·621(6)

NbI_4: 3·43(7), 3·26(8), 3·04(10), 2·96(8), 2·38(8), 1·977(9), 1·835(7), 1·699(6), 1·678(8), 1·266(6)

NbI_3: 6·7(9), 3·36(10), 2·96(9), 2·36(7), 1·907(6), 1·857(6), 1·692(6), 1·659(5), 1·606(5).

Patterns of mixtures from $NbI_{2\cdot8}$ to $NbI_{3\cdot3}$ showed a measurable expansion in the distances for $NbI_{2\cdot8}$ over NbI_3; phases of variable composition have been observed for the corresponding chloride system.[5]

[5] H. SCHÄFER *Angew. Chem.* **67**, 748 (1955).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 210 to 212. Pergamon Press Ltd., London

THE α-FURILDIOXIME COMPLEX OF RHENIUM

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(*Received* 7 *June* 1957)

Abstract—A reduced valence state of rhenium forms a chelate with furildioxime. Qualitative experiments on the complex suggest that it is similar to the nickel(II)– and palladium(II)–dioxime complexes.

A REDUCED valency state of rhenium forms relatively stable, intensely coloured chelates with certain dioxime reagents, e.g. dimethylglyoxime,[1] α-benzil-dioxime,[2] and α-furildioxime.[3] Although these chelates have formed the basis of spectrophotometric methods for rhenium, little is known concerning their nature.

A detailed study of the rhenium–furildioxime complex was conducted. Although this investigation did not lead to positive conclusions concerning the structure and rhenium valency state of the rhenium–furildioxime complex, the results are being reported, since they appear pertinent to the chemistry of rhenium and also to the general topic of dioxime complexation.

EXPERIMENTAL

Attempts at formation of the solid complex

Attempts to prepare the pure solid rhenium–furildioxime complex for precise analytical measurements were unsuccessful. An impure precipitate of the rhenium–furildioxime complex formed when perrhenate, furildioxime and tin(II) chloride were mixed in dilute hydrochloric acid. A major contaminant of this precipitate was the α-diketone, furil. Solvent extraction, recrystallization and chromatography were unsuccessful in purifying the precipitate. Evidence suggested that the purification techniques were not successful, partly because of simultaneous decomposition of the complex. Nevertheless, the composition of the solid was sufficiently good to obtain qualitative information about the nature of the rhenium–furildioxime complex.

Stability of the complex

The absorbance at 530 mμ from a weighed amount of impure solid dissolved in acetone was used as a measure of stability. The rhenium–furildioxime complex was stable for at least 1 month when kept dry, but it deteriorated rapidly in a humid atmosphere. The complex decomposed slowly in acetone solution; water in the acetone increased the rate of decomposition.

* Present address: Research Department, Standard Oil Co. of Indiana, Whiting, Indiana.

[1] M. B. TOUGARINOFF *Bull. Soc. Chim. Belge* **43**, 111 (1934).

[2] S. TRIBALAT *C.R. Acad. Sci., Paris* **224**, 469 (1947).

[3] V. W. MELOCHE, R. L. MARTIN and W. H. WEBB *Analyt. Chem.* **29**, 529 (1957).

Spectrophotometric studies

Previous work in this laboratory, by LARSON,[4] suggested that one molecule of the complex contained one rhenium atom and two dioxime molecules. These conclusions were reached after an analysis of spectrophotometric data with an extension of the BENT and FRENCH method.[5] Since dioxime complexes characteristically involve one metal ion and two dioxime ligands,[6] LARSON's conclusions appear reasonable and likely. Thus, the main question remaining concerned the rhenium valence state in the complex, and indirect efforts were made to resolve this question.

Attempts at formation of the complex from other rhenium valence states

Perrhenate is reduced by tin(II) chloride to rhenium(V) and finally to rhenium(IV)[7] under conditions similar to those used in the formation of the rhenium–furildioxime complex.[3] This would suggest that either rhenium(V) or rhenium(IV) was involved in the dioxime complex. However, standard solutions of rhenium(V) and rhenium(IV), and solutions containing mixtures of the two valence states at various hydrochloric acid concentrations, did not form the complex upon addition of furildioxime. Addition of tin(II) chloride to these solutions, however, produced the intensely coloured rhenium–furildioxime complex. The complexation from rhenium(IV) after addition of tin(II) chloride suggested that the complex contained rhenium with a valence state of less than four. That tin(II) chloride functions as a reductant and is not part of the complex is shown by complex formation with other reducing agents, i.e. vanadium(II) and chromium(II).

In order to establish whether the complex contained divalent or trivalent rhenium, attempts were made to prepare the complex from rhenium(III) trichloride. The complex did not form when furildioxime was added to an acid solution of rhenium(III) trichloride, and subsequent addition of tin(II) chloride also failed to bring about complex formation. This failure may have been due to the stability of rhenium(III) trichloride in acid solution.[8] When furildioxime was added to a neutral solution of rhenium(III) trichloride, a small yield (about 10 per cent) of the complex was obtained, which could be explained by several approaches, e.g. oxidation or disproportionation. Therefore, no conclusions concerning the rhenium valence state could be made from these experiments.

The intensely coloured rhenium–furildioxime complex did form upon air oxidation of an acid solution of rhenium(I) in the presence of the dioxime. Quantitative yields were not obtained, but the yield became higher as the concentration of furildioxime was increased.

Moving boundary experiments

In order to establish whether the complex possessed a charge, moving-boundary experiments were performed. The measurements were made in a Tiselius cell, using acetone–water and methanol–water mixtures containing the complex, with either sodium chloride or hydrochloric acid as the supporting electrolyte. On application

[4] W. J. LARSON Ph.D. Thesis, University of Wisconsin, (1950).
[5] A. E. BENT and C. L. FRENCH *J. Amer. chem. Soc.* **63**, 437 (1941).
[6] H. DIEHL *The Application of the Dioximes to Analytical Chemistry*. G. F. Smith Chemical Co., Columbus, Ohio (1940).
[7] S. TRIBALAT *Ann. Chim.* **4**, 289 (1949).
[8] W. BLITZ, W. GEILMANN and F. W. WRIGGE *Liebigs Ann.* **511**, 301 (1934).

of current through the solution in either direction, no migration of the intense purple colour toward the electrodes was observed, indicating that the rhenium–furildioxime complex was uncharged.

DISCUSSION

A comparison of the solubility and ionic character of the rhenium–furildioxime complex with other metal–dioxime complexes is of considerable interest. Most metal–dioxime complexes involve divalent metal ions,[6,9] however, a number of trivalent metal ions also form dioxime complexes,[6,10,11] e.g. cobalt(III), rhodium(III) and bismuth(III).

The trivalent metal–dioxime complexes are typically soluble in water and are generally of the type $[M(DH)_2X_2]^-$ and $[M(DH)_2A_2]^+$, where X = Cl^-, Br^- or I^-, DH_2 = dioxime, and A = amine.[10,11,12] On the other hand, the typical divalent (nickel(II) and palladium(II)) metal–dioxime complexes are of the type $(MDH)_2$; they are insoluble in water and are fairly soluble in organic solvents. From the solubility aspect, the rhenium complex resembles the divalent complexes. This similarity is extended by the neutrality of the rhenium complex in solution as shown by the moving-boundary experiments. Trivalent rhenium (with two dioxime molecules for each rhenium) would give a charged complex unless anion co-ordination occurred. Anion co-ordination in the complex seems unlikely, because the complex forms when perchlorate is the only anion present, and also because the position of the absorption maximum of the complex is not dependent on the anion present.[13]

The evidence brought forth in the preceding paragraphs enable one to make an "educated guess" that the rhenium complex possesses the same valence state and structure as the nickel(II)–and the palladium(II)–dioxime complexes. Obviously, the evidence does not permit positive conclusions.

The good possibility that the rhenium–furildioxime complex contains divalent rhenium makes it a very interesting compound, since there are very few,[14,15] if any compounds proved to involve rhenium(II).

Acknowledgements—The authors are indebted to the Dow Chemical Co. for financial assistance in this project. The authors also wish to thank DONALD D. DONERMEYER for conducting the moving boundary experiments.

[9] H. F. WALTON *Principles and Methods of Chemicals Analysis* p. 86. Prentice-Hall, New York (1952).
[10] L. CAMBI and L. MALATESTA *Gazz. Chim. Ital.* **69**, 547 (1939).
[11] F. P. DWYER and R. S. NYHOLM *J. roy. Soc. N.S.W.* **78**, 266 (1946); **79**, 126 (1946).
[12] V. V. LEBENDENSKI and I. A. PEDEROV *Ann. Sect. Platine, Leningr.* **15**, 27 (1938).
[13] R. L. MARTIN Ph.D. Thesis, University of Wisconsin, 1957.
[14] N. V. SIDGWICK *The Chemical Elements and Their Compounds* p. 1292. Oxford Press, London (1950).
[15] V. TRONEV and S. BONDIN *Dokl. Akad. Nauk SSSR* **86**, 87 (1952).

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THE ABSORPTION SPECTRUM OF AQUEOUS CURIUM (III)*

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Abstract—The absorption spectrum of aqueous curium (III) has been studied in 0·04 N $HClO_4$, using the isotope ^{244}Cm. Three prominent absorption peaks have been discovered at 3754 Å, 3812 Å and 3965 Å, in addition to absorption in the far ultra-violet. These same peaks are found in HCl, HNO_3 and H_2SO_4 solutions. The general characteristics of the spectra in these three acids and some general observations on the radiation decomposition of aqueous curium solutions are reported.

THE absorption spectrum of curium (III) in 0·5 N HCl has been reported to be confined to the region below 4500 Å with an intense peak near 3300 Å[1a,1b]. In $HClO_4$ no characteristic peaks were observed; the spectrum was reported to be limited to general absorption below ca. 3000 Å[2] The work described in references 1 and 2 utilized the intensely active α-emitter ^{242}Cm, $t_{\frac{1}{2}} = 162{\cdot}7$ days,[3] $E_\alpha = 6{\cdot}1$ MeV.[4] A double peak between 3765 and 3815 Å was observed in the absorption spectrum when we attempted to repeat the early work with ^{242}Cm in $HClO_4$, but the intensities of the lines were so weak that a positive assignment to curium could not be made.

It was decided to re-examine the spectrum of curium, using the α-emitting isotope ^{244}Cm, $t_{\frac{1}{2}} = 18{\cdot}4$ years,[5] $E_\alpha = 5{\cdot}8$ MeV.[4] It was found that such experiments were simultaneously in progress at the Los Alamos Scientific Laboratory (L.A.S.L.) and the Argonne National Laboratory (A.N.L.), each using curium with a different chemical history.

EXPERIMENTAL

The ^{244}Cm was obtained by intense neutron bombardment of ^{239}Pu in the Materials Testing Reactor. The curium was isolated from fission products, plutonium, and transcurium elements by means of a series of anion and cation resin columns. After four column separations, the curium samples were still contaminated with americium and a small amount of rare earths. At L.A.S.L., final separation from americium was effected by alkaline (3 M K_2CO_3) oxidation to $KAmO_2CO_3$,[6] using ozone. Curium

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1a] L. B. WERNER and I. PERLMAN *J. Amer. chem. Soc.* **73**, 5215 (1951).
[1b] L. B. WERNER and I. PERLMAN *The Transuranium Elements: Research Papers.* National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, Paper No. 22.5 McGraw-Hill, New York (1949).
[2] W. W. T. CRANE *University of California Radiation Laboratory Report*, UCRL–1220 (1951).
[3] R. A. PENNEMAN, R. B. BEVIN, S. E. STEPHANOU and L. H. TRIEMAN Los Alamos Scientific Laboratory. Private communication.
[4] F. ASARO, S. G. THOMPSON and I. PERLMAN *Phys. Rev.* **92**, 694 (1953).
[5] A. M. FRIEDMAN, A. L. HARKNESS, P. R. FIELDS, M. H. STUDIER and J. R. HUIZENGA *Phys. Rev.* **95**, 1501 (1954).
[6] J. P. NIGON, R. A. PENNEMAN, E. STARITZKY, T. K. KEENAN and L. B. ASPREY *J. phys. Chem.* **58**, 403 (1954).

is not oxidized under such conditions.[7] Curium was separated from the last traces of rare earths by using a 20 per cent ethanol solution saturated with HCl as an eluant[8] from a Dowex-50 cation resin column. A similar procedure was used at A.N.L., effecting the americium oxidation with persulphate in 0·1 N HNO_3 at 80°C.[7] The final rare-earth separation also made use of a Dowex-50 resin column, but 13 M HCl was used as the eluant.[8]

Spectrographic analysis of the curium fractions showed all rare earths to be below the limits of detection; this precluded the possibility that rare-earth absorption spectra would be observed under the conditions used to measure the curium spectrum. The total impurities (mostly calcium and aluminum) were $<1{\cdot}5$ per cent by weight. Alpha-pulse analysis showed no α-emitters present other than curium ($<5\alpha$ per cent ^{242}Cm). The curium absorption spectrum was observed before and after chemical treatment during various stages of the purification. The characteristic peak of Am(III) at 5027 Å was absent from the spectrum after purification. No change was observed in the peaks attributed to curium in either the relative peak heights or the absolute magnitudes relative to total curium present during the course of purification.

Absorption measurements were made with two instruments: a Cary recording spectrophotometer, Model 14M with quartz cells 2·5 cm long; and a Beckman DU spectrophotometer with standard 1 cm quartz cells. The cell compartment of the former was thermostated at 25°C; the latter was run at room temperature of ca. 25°C.

TABLE 1.—CURIUM ABSORPTION MAXIMA

λ in Å	ε (molar)
3754	28·2
3812	31·0
3965	52·9

Both instruments were provided with special cell holders to prevent the spread of contamination in the event of leakage of the active material. Blanks were run on the various acid solutions to insure that none of the observed absorption was due to an impurity. The spectrophotometers were calibrated in the 4000 Å region by using the 4062·5 Å line of hydrogen and all reported wavelengths include the necessary corrections to this calibration.

RESULTS

Fig. 1 shows a typical tracing of the spectrum of ^{244}Cm in 0·04 N $HClO_4$. The wavelengths and extinction coefficients of the three prominent peaks are given in Table 1. Absorption at the three principal maxima was found to obey Beer's law. The small peak at ca. 2900 Å and the two peaks near 4500 Å were considered too weak to permit an accurate evaluation of the extinction coefficient. No structure was found between 4700 Å and 11,000 Å. From 11,000 Å to 12,500 Å, some slight irregularities

[7] S. E. STEPHANOU and R. A. PENNEMAN *J. Amer. chem. Soc.* **74**, 3701 (1952).
[8] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG *J. Amer. chem. Soc.* **76**, 6229 (1954).

were observed, but they were weak and could have resulted from a cell mismatch, since water absorbs strongly in this region.

The spectrum of Cm(III) in $\leqslant$1 N HCl, HNO_3 and H_2SO_4 closely resembled that in $HClO_4$. In HCl and HNO_3 there was an increase in the molar extinction coefficient of the peaks at 3754, 3812 and 3965 Å, with increasing acid concentration, and this was accompanied by general increased absorption in the region 2200–3400 Å; the intense nitrate ion absorption limited observation in that medium below 3400 Å. In $\geqslant$6 N HCl two additional peaks were observed; a very broad peak in the region

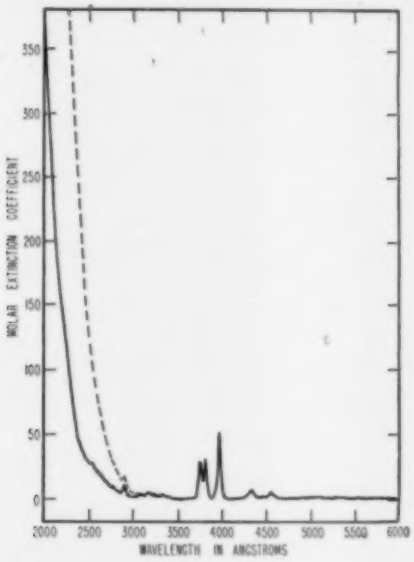

FIG. 1.—Absorption spectrum of 0·000944 M Cm in 0·04 N $HClO_4$
——— 0·37 hr after preparation
····· 98·7 hr after preparation

3000–3700 Å with centre near 3300 Å and a much more distinct peak centred near 2690 Å. Both increased with increasing HCl concentration. The situation was complicated by the fact that the molar extinction coefficient of these peaks also increased as a function of time, indicating that they may not have been characteristic of Cm(III) but of the effect of intense α-radiation on chloride ion. Radiation decomposition was also observed in >6 N HNO_3, H_2SO_4, and $HClO_4$. The absorption spectrum of Cm(III) in HCl, HNO_3 and H_2SO_4 will be the subject of a further communication from these laboratories.

DISCUSSION

It can be seen in Fig. 1 that the strong absorption in the ultra-violet region reported previously[2] for curium in $HClO_4$ changes with time. This change is believed due to the growth of H_2O_2 in the system as a result of the α-induced decomposition of water. The absorption spectrum of H_2O_2 in aqueous solution has been shown to be continuous, extending from 3000 to 3100 Å toward the far ultra-violet region with no structure of any kind.[9] Some calculations were made relating the rate of change of

[9] H. C. UREY, L. H. DAWSEY and F. O. RICE *J. Amer. chem. Soc.* **51**, 1371 (1929).

optical density (at 2200 Å) with time to the growth of H_2O_2 from α-radiation as observed by LEFORT.[10] The observed rate of change of optical density for the curium system is in reasonable agreement with the rate of growth of H_2O_2 reported by LEFORT. These observations suggest that the previous workers,[2] who did not have ^{241}Cm available at the time of their research, were actually observing peroxide absorption in the region <3000 Å.

In addition to the production of H_2O_2, decomposition of the solvent acids has been observed, and it is this effect that may explain the results of WERNER and PERLMAN.[1a,1b] In the present work in HCl the rate of increase in optical density of a peak centred near 3300 Å was a direct function of chloride ion concentration. In 10 N HCl immediately after sample preparation the three peaks attributed to curium appeared as small perturbations on the larger peak with centre near 3300 Å. As the 3300 Å peak increased, the peaks near 4000 Å were lost. The concentrations of curium used in the earlier work[1a,1b] were equal to or greater than those in the present investigation, but the specific activity was a factor of 40 greater, thus the more intense α-activity may have given rise to an appreciable decomposition of the more dilute HCl.

In $\leqslant 1$ N HCl solutions of curium the region near 2400 Å showed very little change over a period of several hours, in harmony with the observation of ANTA[11] that HCl at concentrations between 0·05 and 0·8 N inhibits the growth of peroxide in solutions containing α-emitting elements. Thus it may be that the strong ultra-violet absorption observed by WERNER and PERLMAN[1b] below 3000 Å was also due to solvent acid decomposition rather than to the production of H_2O_2.

CONCLUSIONS

Three prominent peaks have been discovered in the absorption spectrum of Cm(III). Assignment of this structure to Cm(III) was made for the following reasons: (1) The position and relative magnitude of the peaks were unchanged through several chemical manipulations, (2) independent work at two laboratories led to identical results, (3) no elements known to contribute sharp rare-earth-like absorption in this region could be detected spectroscopically in the purified material.

The fact that the peaks reported in the present communication as characteristic of Cm(III) were not observed in earlier studies may be attributable to strongly absorbing species produced by radiation decomposition of the solvent that override the curium peaks.

All of the acids used in the present investigation (HCl, $HClO_4$, HNO_3, and H_2SO_4) were sufficiently decomposed by the intense α-activity of the curium to give rise to one or more species that absorbed strongly in the ultra-violet region.

[10] M. LEFORT *J. Chim. phys.* **51**, 351 (1954).
[11] M. C. ANTA *J. Chim. phys.* **51**, 401 (1954).

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REACTION OF THIOCYANATOPENTAMMINECOBALT (III) ION WITH CHROMOUS ION*

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Abstract—Contrary to expectation, the reaction of chromous ion with thiocyanatopentamminecobalt (III) ion gives N-thiocyanatochromic ion. Radio-tracer studies indicate extensive exchange with free thiocyanate ion during the reaction. A tentative explanation is presented.

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SINCE the X-ray investigation of Reinecke's Salt by SAITO, TAKEUCHI and PEPINSKY,[1] which showed that a chromium-N-thiocyanate bond system is obtained in this salt, it has been assumed [see, for example, the work of KING[2,3]] that all complex ions of chromium (III) with the thiocyanate ligand contain this same *iso*thiocyanato bond system. The interesting possibility then arises of making an S-thiocyanato-chromium (III) complex.

This synthesis was attempted by reducing the thiocyanatopentamminecobalt (III) ion with chromous ion. TAUBE[4] has shown that in this reaction the thiocyanate ion acts as a bridge for the electron transfer, and is then itself transferred to the chromium. Now, it is known[5] that cobalt also forms an N-thiocyanato complex-ion, and if we assume that TAUBE's bridged-activated complex is of the form $[Co—NCS—Cr]^{+4}$ and not of a form such as

$$[Co—\underset{\displaystyle \underset{\displaystyle S}{|}C}{N}—Cr]^{+4},$$

we would expect to find a $[Cr—SCN]^{++}$ system in the new chromium (III) ion.

The spectra of the solution resulting from this redox reaction has been studied and compared with that of the known N-thiocyanatopentaquochromium (III) ion. Tracer studies were also carried out in an attempt to elucidate the mechanism of this reaction.

PREPARATION OF COMPOUNDS

$[Co(NH_3)_5NCS][NCS]_2$ was prepared from $[Co(NH_3)_5NO_3][NO_3]_2$[6] by boiling 8 g for several minutes in 150 ml of a saturated solution of ammonium thiocyanate, cooling, and filtering. The perchlorate salt was made by dissolving portions of this salt in just enough water to complete solution; keeping this solution cool in ice, sodium perchlorate was added with stirring until the solution turned a

* Taken from the Sc. B. thesis of R. L. C., in which further details may be found.

[1] Y. SAITO, K. TAKEUCHI and R. PEPINSKY *Z. Krist.* **106**, 476 (1955).
[2] E. L. KING and E. B. DISMUKES *J. Amer. chem. Soc.* **74**, 1674 (1952).
[3] J. T. HOUGEN, K. SCHUG and E. L. KING *J. Amer. chem. Soc.* **79**, 519 (1957).
[4] H. TAUBE *J. Amer. chem. Soc.* **77**, 4481 (1955).
[5] M. LINHARD, H. SIEBERT and M. WEIGEL *Z. anorg. Chem.* **278**, 287 (1955).
[6] W. G. PALMER *Experimental Inorganic Chemistry* p. 535. Cambridge University, Cambridge (1954).

cloudy red, and the dark-pink precipitate of $[Co(NH_3)_5NCS][ClO_4]_2$ was then filtered off.

$[Co(NH_3)_5NC^{14}S][ClO_4]_2$ was made by adding radiothiocyanate to the solution of ammonium thiocyanate and $[Co(NH_3)_5NO_3]^{++}$ before it was boiled. The remaining procedure was the same as above.

Sodium radiothiocyanate: Sodium cyanide-^{14}C was obtained as such from the New England Nuclear Corp., Boston, Mass., and converted into sodium radiothiocyanate by the method of ADAMSON and WILKINS[7]

EXPERIMENTAL PROCEDURE

The apparatus for preparing, storing, and dispensing the solution of chromous ion, and the reaction flask were similar to those of TAUBE and MYERS.[8] The experimental procedure was also the same, except that the reaction solution was stirred with the flow of nitrogen. Zinc amalgam was made as directed by VOGEL.[9] It was found inconvenient to oxidize the excess chromous ion in the reaction flask with hydrogen peroxide, as oxygen was evolved when the solution was passed through the ion-exchange column, creating "air" pockets. No adverse effects were noticed if the chromous ion was oxidized by opening the flask, at the end of the reaction, to the atmosphere. The thiocyanatocobalt salt was found to be only slightly soluble, so 50 ml of water were saturated with the salt, and then introduced into the reaction flask. The solution was less than or about 0·015 M.

After the redox reaction was over (10 min were allowed), the solution was run through the ion-exchange column in the hydrogen form. The thiocyanatochromium (III) ion was eluted with 1 N perchloric acid by the method of KING and DISMUKES;[2] it was assumed that the S- and N-thiocyanatochromium (III) species would behave similarly in the elution procedure, and that no isomerization would be induced by the ion-exchange procedure. Preliminary experiments had shown that no cobaltous or oxidized chromous (polynuclear) species were eluted by 1 N perchloric acid. The ion-exchange resin was Dowex 50-X4, 100–200 mesh.

The spectrum of the chromium species eluted with 1 N perchloric acid was then observed on a Beckman DU spectrophotometer with 10 mm Pyrex cells. The chromium complex was then destroyed with sodium hydroxide and hydrogen peroxide added to oxidize the chromium to chromate. The data of TSUCHIDA and KOBAYASHI[10] on the spectrum of the chromate ion were used in the standardization of the chromium-containing eluant solutions.

The reaction between chromous ion and the radioactive thiocyanatocobalt salt was carried out as above, except that the solution was first made 0·03 M in stable thiocyanate. After reaction, the solution was run through the ion-exchange column, and the excess thiocyanate was precipitated with silver nitrate. The silver thiocyanate was collected and then a count of the radioactivity was taken.

The 1 N perchloric acid solution of eluted thiocyanatochromic ion was then made basic (pH 10) with sodium hydroxide, then acid (pH 2) with perchloric acid, and then silver nitrate was added. A precipitate of silver thiocyanate was obtained immediately; it was collected and also counted for radioactivity.

RESULTS AND DISCUSSION

The absorption spectrum of the thiocyanatopentaquochromium (III) ion eluted from the ion-exchange column was observed and found to be identical to that reported by KING and DISMUKES[2] for the usual N-thiocyanatochromic ion. If the complex contained an S-thiocyanato chromium bond, we would expect a shift in the wavelength of maximum absorption and/or a change in extinction coefficient; neither of these effects was observed. It would therefore seem safe to conclude that this sulphur–chromium bond, if formed, is unstable and isomerizes rapidly. If

[7] A. W. ADAMSON and R. G. WILKINS *J. Amer. chem. Soc.* **76**, 3379 (1954).
[8] H. TAUBE and H. MYERS *J. Amer. chem. Soc.* **76**, 2103 (1954).
[9] A. I. VOGEL *Practical Organic Chemistry* (2nd Ed.) p. 194. Longmans Green, London (1948).
[10] R. TSUCHIDA and M. KOBAYASHI *Bull. chem. Soc. Japan.* **13**, 471 (1938).

excess chromous ion were to attack the nitrogen end of the chromium S-thiocyanate in a redox reaction of the type

$$Cr—SCN^{++} + Cr^{++} \rightarrow [Cr—SCN—Cr]^{+4} \rightarrow Cr^{++} + Cr—NCS^{++}$$

the result would be just such an isomerization.

The data obtained in the tracer studies show that a greater fraction of radioactivity was present in the free thiocyanate ion in solution than was present in the chromium complex. The ratio (counts/min per counts/min) of free thiocyanate over bound thiocyanate was successively in the range of 20 : 1 on up to 40 : 1. Thus the radio-thiocyanate, which presumably acted as a bridge for the electron transfer and became bound to the chromium through sulphur, was replaced by the excess stable thiocyanate of the solution upon isomerization. A direct aquation of the S-thiocyanato complex followed by replacement of a water by thiocyanate to form an N-thiocyanato complex is not possible, as the hexaquochromic ion is known to be substitution inert,[8] as is also the N-thiocyanato complex.

It appears, therefore, that the isomerization reaction is one of dissociation. The chromium S-thiocyanate bond (which probably is formed) must break and then the ions rejoin to form a new complex ion bound through the nitrogen. A short but finite lifetime in solution for a pentaquochromium ion is postulated, as is the ability of the thiocyanate ion to successfully compete with water for the sixth position in the co-ordination sphere of chromium. Ion-pair formation between the postulated pentaquochromium ion and thiocyanate ion appears possible. Such a ion pair might prevent a water molecule from entering the co-ordination sphere as the sixth ligand and could re-arrange itself to form the normal N-thiocyanate complex as was found.

The results obtained are presented in this incomplete form, as further work here is not feasible. The data are very suggestive and it is hoped that independent substantiation will be possible elsewhere.

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SYNTHETIC INORGANIC ION-EXCHANGE MATERIALS—I
ZIRCONIUM PHOSPHATE

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Abstract—This paper describes some of the properties of zirconium phosphate as an example of a class of very stable synthetic inorganic ion-exchange materials, which may be prepared in granular form suitable for column operations. It exhibits properties typical of a polyfunctional, weakly acid cation exchanger, with capacities up to ~5 mequiv/g in alkaline solution. Materials with a low phosphate : zirconium ratio possess in addition anion-exchange properties due to anions retained in the structure from the original zirconium salt. Cations may be exchanged rapidly and reversibly upon acid phosphate groups in the gel structure. Distribution coefficient measurements for alkali metal and alkaline earth ions have been made, and the material shows promise for separation purposes; uptake is reduced at elevated temperatures owing to hydrolysis. The stability of the material towards water at temperatures up to 300°C suggests its possible use for water treatment in high-temperature systems, as well as other possibilities.

A WIDE variety of uses has been found for synthetic organic ion-exchange resins and for zeolitic inorganic exchangers, and new uses are constantly being suggested; considerable quantities of these materials are used industrially. Their use is however limited by virtue of their limited stability under various conditions; for example, the zeolites are unstable in mildly acid solutions, while the organic resins break down at high temperatures. In addition, while the radiation stability of organic resins is usually sufficient for use in the chemical processing of radioactive solutions, exposure to radiation doses characteristic of the processing of very highly active solutions causes significant changes in capacity and selectivity, presumably by hydrolysis of functional groups, chain scission, and changes in degree of cross-linking.[1] There is therefore a need for ion-exchange materials possessing a high degree of stability towards extremes of temperature and ionizing radiation dose, and possessing appreciable exchange capacity over a wide range of acidity.

Among the possible uses for such materials are the following ones:

(a) The treatment of high-temperature water for removal of corrosion-products and ionic impurities. This application is analogous to boiler-water treatment as practised at present, but without the need to lower temperatures in the treatment cycle in order to prevent resin destruction.
(b) Purification and conditioning of moderator and cooling water in pressurized-water reactors.
(c) Chemical separation and purification in intense radiation fields.
(d) Ion-exchange catalysis of reactions taking place at temperatures at which organic resins are decomposed.

In addition, it is conceivable that in some cases increased specificity may be obtained

[1] G. I. CATHERS *International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, p. 490. United Nations (1956).

compared with the use of organic resins, leading to improvements even under normal operating conditions.

It would be expected that suitable insoluble inorganic materials would be superior in stability to organic polymers; for example, clays such as montmorillonite still exhibit ion-exchange properties in water at 300°C,[2] and the zeolites are known to exhibit reversible exchange at similar temperatures.[3] Unfortunately, these materials are limited in their stability towards acids, and exchange is relatively slow. Cation exchange properties are also possessed by the insoluble acid salts formed by polybasic acids and certain hydrolysable polyvalent cations, and many of these salts are extremely insoluble in most reagents; typical examples are the phosphates, arsenates, tungstates, and molybdates of zirconium, thorium, titanium, and other metals.[4] Preliminary results on zirconium phosphate have been presented elsewhere;[5] the present paper deals with this material in more detail, while later papers will deal with other work in this field.

EXPERIMENTAL

Preparation of granular zirconium phosphate

The product obtained when a phosphate solution is added to a solution of a soluble zirconium salt is normally a viscous, gelatinous precipitate, which settles extremely slowly and is very difficult to filter. Under suitable conditions a filterable, finely-powered product may be prepared,[6] but although this possesses ion-exchange properties its particle size is too small for it to be of use in large-scale column operations. A way was therefore sought to prepare a granular product from the gel which is obtained by the first method. Conditions were chosen which were favourable to gel formation, viz. rapid precipitation from relatively concentrated solutions at room temperature with efficient stirring and rapid addition of the reagents. In most of the preparations, phosphoric acid has been added to a solution of zirconyl nitrate in 1 N nitric acid, but similar products have been obtained using zirconyl chloride in hydrochloric or perchloric acids or zirconium sulphate in sulphuric acid, and by using soluble phosphates instead of phosphoric acid. The order of addition of reagents is unimportant, and both the rate of addition and the stirring-rate may be varied within wide limits, provided that mixing is efficient. Preparation at room temperature is preferred, although similar products have been obtained at 50°C; with increasing temperature there is less tendency to form clear gels. Increase in phosphoric acid concentration beyond 10 per cent by volume leads to powdery products, presumably due to dehydration by the acid, since comparable phosphate ion concentrations derived from alkali phosphates are without harmful effect.

When first prepared, the gelatinous precipitate cannot easily be filtered or washed, but it may be coagulated either by addition of alkali to remove excess acid or by continued washing with water followed by decantation. It may then be filtered under suction and washed free of soluble salts until it has a pH of approximately 3. Coagulation by alkali occurs suddenly when the last trace of free acid is neutralized; presumably the gel consists of negatively-charged particles stabilized by H^+ ions in the presence of free acid and flocculated by OH^- ions after neutralization. After drying under suction, the gel is dried in an oven until it shrinks and breaks down in the manner of silica gel; this has been done at temperatures ranging from 30 to 300°C. At the higher temperature a physically more stable product is obtained, with some loss in exchange capacity (see below).

The product obtained by this preliminary drying usually consists of agglomerates having visible strain-lines, cracks, and air-bubbles; on immersion in water this breaks down vigorously and noisily, with evolution of heat and escape of entrapped air, to give a granular product which after subsequent drying does not break down when immersed in water at the same temperature. If immersed

[2] S. Goldsztaub and R. Wey *C.R. Acad. Sci., Paris* **243**, 261 (1956).
[3] R. M. Barrer *et al. J. chem. Soc.* 2158 (1948); 1267 (1951); 1561 (1952); 1466, 1879, 4029, 4035 (1953); 4641 (1954); 2838 (1955).
[4] K. A. Kraus and H. O. Phillips *J. Amer. chem. Soc.* **78**, 694 (1956); K. A. Kraus, T. A. Carlson and J. S. Johnson *Nature, Lond.* **177**, 1128 (1956).
[5] C. B. Amphlett, L. A. McDonald and M. J. Redman *Chem. & Ind. (Rev.)* 1314 (1956).
[6] E. M. Larsen, W. C. Fernelius and L. L. Quill *Analyt. Chem.* **15**, 512 (1943).

in water at a higher temperature some further breakdown occurs; the particle size distribution appears to be dependent upon the temperature of the water used. The equilibrium particle size distribution also appears to be displaced in the direction of larger particle size as the temperature of drying is increased; material dried at 300°C is little affected even on prolonged treatment with water under pressure at 300°C.

Details of the preparation from zirconyl nitrate and phosphoric acid are as follows:[7] 540 ml of H_3PO_4 solution (54·2 g/l.) was added rapidly to 556 ml of a well-stirred solution of $ZrO(NO_3)_2$ in 1 N HNO_3 (107 g $ZrO(NO_3)_2$, $2H_2O$/l). After stirring for 10–15 min the gelatinous suspension was washed several times with large volumes of distilled water; after each washing it was allowed to stand, and the supernatant liquid was decanted when the suspension had settled. After several washes the suspension settled well; it was then filtered under suction, washed until free from nitrate ions and excess acid, and dried in air at 30°C. The dried product was then broken down in water at room temperature and dried again. Yield: 60·0 g. The supernatant liquid in this preparation was found to contain excess phosphate ion but no soluble zirconium ions. By varying the ratio of the two reactants, products may be obtained in which the ratio of phosphate to zirconium varies over a fairly wide range; at the lowest values studied, the supernatant solution contained zirconium ions but no phosphate.

pH-Titration curves

These were determined using standard techniques.[8] 0·5 g of zirconium phosphate was equilibrated with 75 ml of a solution containing NaCl and NaOH, the total sodium concentration being 0·1 N. After standing for 1 week, with intermittent shaking, samples of the supernatant liquid were analysed for residual sodium content (using an EEL flame photometer), and their pH was measured on a Doran pH-meter. Measurement of sodium uptake by stripping the washed exchanger with acid gave less reliable results, owing to the loss of sodium on washing with water (see below).

Distribution coefficients and exchange capacities

Batch distribution coefficients were measured by equilibrating weighed amounts of material with known volumes of suitable solutions, followed by analysis of the supernatant liquid; the ratio of solution to solid was usually 100 ml/g, and data were obtained either from duplicate runs at different equilibration times or from rate runs to equilibrium. Saturation exchange capacities were measured either from column runs or from repeated batch equilibration until further uptake was negligible. Both breakthrough and elution curves were plotted in the column experiments, and the capacity was calculated from the areas over and under these curves respectively, after correcting for the previously determined pore volume.

Analytical methods employed included the use of ^{137}Cs as tracer for caesium, flame photometry for Li, Na, K, and Sr, EDTA titrations for Mg, Ca, and Ba, precipitation of Rb_2SnCl_6 for Rb, and distillation with alkali followed by titration for NH_4.

Rates of exchange

For periods upwards of 5 min, 0·1 g of material was stirred with 10 ml of solution in a 20 ml centrifuge tube, after which the cation was estimated in the supernatant solution. For shorter periods, stirring was carried out in a No. 2 sintered-glass funnel fitted to a filter-tube, the exit tube of which could be connected via a three-way stopcock either to vacuum or to a compressed-air supply. During a run a small flow of compressed air was maintained to prevent drainage of the solution; at the chosen time the stopcock was reversed and the solution drained rapidly by suction. Drainage time was approximately 2 sec, and good reproducibility could be obtained at times down to 15 sec.

PHYSICAL AND CHEMICAL PROPERTIES

The material prepared by the method described above is a hard, glassy gel, provided that the mole ratio of phosphate to zirconium in the starting materials is greater than 0·5; below this value, colloidal solutions appear to be formed. Above

[7] C. B. AMPHLETT Pat. Appl. No. 17722/56 (1956).
[8] N. E. TOPP and K. W. PEPPER *J. chem. Soc.* 3299 (1949).

this value, gels may be obtained with a wide range of phosphate : zirconium ratio, all of which show ion-exchange properties. A range of particle sizes is obtained from +20 B.S.S. mesh downwards, the equilibrium particle size distribution moving towards larger mesh sizes as the drying temperature is increased. The water content of the gel, measured by drying to constant weight, varies from 20 to 25 per cent by weight. X-ray examination indicates an amorphous structure.

The product is insoluble in most reagents, and may be refluxed for several hours in concentrated nitric acid or in 2 N NaOH without physical breakdown; at the end of this treatment the capacity is not altered significantly, although in alkaline solution

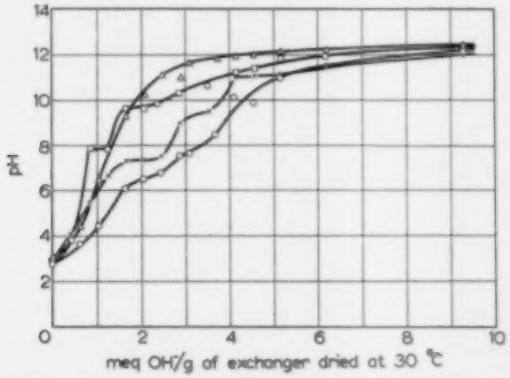

FIG. 1.—Titration curve for zirconium phosphate preparations with varying PO_4/Zr ratio.
Ordinates: pH units. Abscissae: mequiv. OH^-/g of dry exchanger (30°C).
Legend: ○ Phosphate: Zr mole ratio in reagents = 2·5 : 1
× Phosphate: Zr mole ratio in reagents = 1·4 : 1
△ Phosphate: Zr mole ratio in reagents = 0·9 : 1
⊡ Phosphate: Zr mole ratio in reagents = 0·5 : 1
Conditions: 0·5 g of exchanger equilibrated with 75 ml 0·1 N (NaCl + NaOH).

there is a slight release of phosphate to solution. There is little breakdown after refluxing in water for several weeks, and samples have been treated with water at 300°C for up to 1 week without appreciable production of fines; the product suffers slight breakdown, but is still granular, and the extent of breakdown is considerably less for material dried at high temperatures. After treatment with water at such temperatures, the material shows evidence of efficient uptake of corrosion-products from the metal autoclave; the granules may be grey or green in colour, and iron and nickel may be removed from them with difficulty by treatment with hot, concentrated acids. Possibly the metals are incorporated as oxides into the gel structure. A similar uptake of corrosion-products has been observed after treatment with very dilute sulphuric acid solutions (10^{-2}–10^{-4} N) in a stainless-steel autoclave at 200–250°C.

The pH-titration curve for granular zirconium phosphate (Fig. 1) shows it to possess several dissociable hydrogen atoms with a range of values of pK_a. At low pH the gradual increase in pH as alkali is added suggests that there may be overlapping values of pK_a in this region, while at higher pH there are better-defined inflexions due to more weakly acid groupings. Although these cannot be definitely attributed to known values of pK_a for individual polybasic phosphoric acids, there are certain similarities to both simple and condensed members of this class. In view of the acidity of the solutions used in the preparation, it might be expected that a range of acid

phosphate or condensed phosphate groups could be present. The existence of several inflexions may not indicate an equal number of chemically different acid phosphate groups, since it is possible that the pK_a of any one acid phosphate group might depend upon its position in the gel network.

Variations have been observed between different batches prepared by the same method, and these are usually most marked in the acid region of the curve; the position of the more weakly ionized groups is much less sensitive to deliberate and adventitious changes in method of preparation. The general pattern is, however, fairly constant, and similar curves are obtained for material prepared from $ZrO(NO_3)_2$.

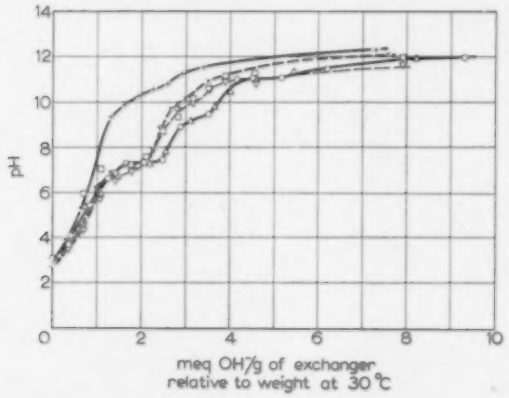

FIG. 2.—Titration curve for zirconium phosphate as a function of drying temperature.
Mole ratio of phosphate to zirconium in reagents = 1·4 : 1.
Ordinates: pH units. Abscissae: mequiv. OH^-/g of exchanger, relative to original weight dried at 30°C.
Legend: ○ Drying temperature 30°C; ▽ Drying temperature 150°C.
△ Drying temperature 50°C; × Drying temperature 200°C.
⊡ Drying temperature 100°C; + Drying temperature 300°C.

$ZrOCl_2$, or $Zr(SO_4)_2$. As would be expected, the reduction in the ratio of phosphate to zirconium produces a more basic product, the curve being successively displaced as this ratio is decreased (Fig. 1). The weaker acid groupings remain relatively unaffected, while there is a progressive loss of the more acid ones; consequently the cation exchange capacity at low pH decreases considerably, while the total available capacity in alkaline solution suffers only a small proportionate reduction (see below). A similar effect is seen if Na_3PO_4 is used instead of H_3PO_4 in the preparation, or if the zirconium solution is added to the phosphate solution instead of vice versa; in the latter instance the effect is much less marked. Before firm conclusions can be drawn it will be necessary to devise a method of preparing samples which are themselves more reproducible in their behaviour from batch to batch.

When material originally dried at 30°C is dried at higher temperatures it loses water, at first reversibly, but at temperatures above 150°C appreciable irreversible water loss is observed; the loss in weight becomes approximately constant at about 300°C, and is not significantly increased at temperatures up to 1000°C. Examination of the pH-titration curves (Fig. 2) for samples of one batch dried at different temperatures between 30 and 300°C shows that between 30 and 50°C there is little change, but that at higher temperatures there is a progressive decrease in acidity involving the

more weakly acid groups, and that this is not reversed on immersing in water. Since the more marked loss of activity at the higher temperatures is accompanied by the onset of irreversible water losses and by loss of capacity in the region of medium pH (see below), the process taking place may involve condensation of acid phosphate groups to form condensed P—O—P structures and further cross-linking.

The hydrogen form of zirconium phosphate imparts an acid reaction to distilled

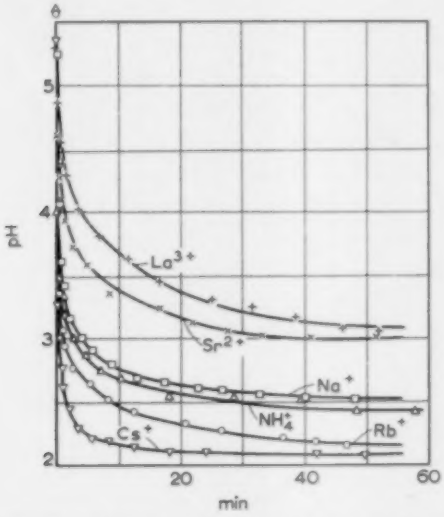

FIG. 3.—Release of hydrogen ion on equilibration of zirconium phosphate with salt solutions.
Ordinates: pH units. Abscissae: min.
Legend: ▽ $CsNO_3$ ⊡ NaCl
○ $RbNO_3$ × $Sr(NO_3)_2$
△ NH_4NO_3 + $La(NO_3)_3$
0·3 g exchanger (PO_4: Zr = 1·4) + 20 ml 0·1 N solution.

TABLE 1.—EQUILIBRIUM pH OF ZIRCONIUM PHOSPHATE IN AQUEOUS SUSPENSIONS

Material	Solution	pH
I Phosphate-excess, prepared from sulphate	Distilled water	3·12
II The same, prepared from nitrate	Distilled water	2·92
III The same, prepared from chloride	Distilled water	3·15
IV Zirconium-excess, prepared from sulphate	Distilled water	2·58
Acid sodium form of I, prepared by treatment with NaCl solution	Distilled water	4·44
Alkaline sodium form of I, by equilibration with NaOH	Distilled water	8·47
I	0·1 N Cs^+ solution	2·0
I	0·1 N Rb^+ solution	2·1
I	0·1 N NH_4^+ solution	2·4
I	0·1 N Na^+ solution	2·5
I	0·1 N Sr^{2+} solution	3·0
I	0·1 N La^{3+} solution	3·1

water when equilibrated with it, due to ionization of the more acid groups; the equilibrium pH is approximately 3·0. When added to a neutral salt solution the pH of the latter falls rapidly at first and then reaches a value lower than that in water alone (Fig. 3), due to liberation of H^+ ion by exchange with the cation in solution. By using different salt solutions a rough affinity series may be drawn up for any given salt concentration, and the results are in fair agreement with results of distribution experiments described below; it will be noted that Sr^{2+} and La^{3+} show a relatively poor affinity, due to the relatively high total salt concentrations favouring H^+ ion

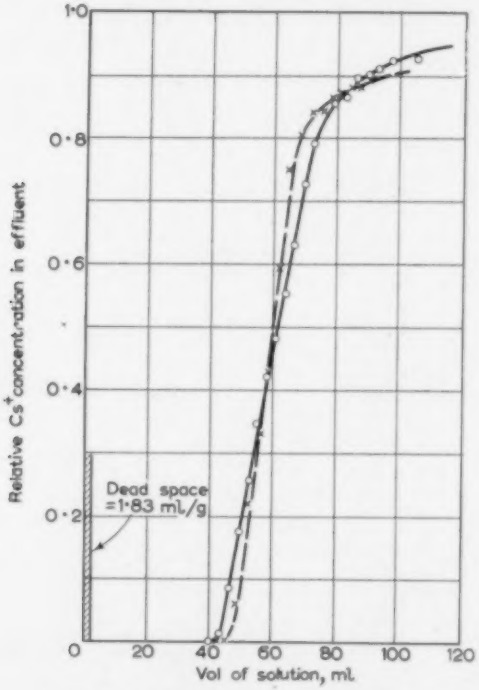

FIG. 4.—Uptake of Cs^+ ions from neutral solution on zirconium phosphate.
Ordinates: relative concentration of Cs^+ in effluent
Abscissae: ml solution/g of exchanger
Legend: ○ 0·0205 N Cs^+, pH 5·6, 20°C.
× 0·0200 N Cs^+, pH 5·5, 56°C.

in the 1 : 2 and 1 : 3 exchange reactions involved in these cases. When saturated with cations from neutral solution (which involves only the more strongly acid groups), the metal forms of the exchanger also give an acid reaction in water, although the equilibrium pH is higher than that of the acid form (Table 1), since the latter is a stronger acid. Replacement of all the exchangeable hydrogen ions by treatment with alkali gives cation forms which have an alkaline reaction in water (Table 1), presumably due to a slight hydrolysis of phosphate analogous to the behaviour of Na_3PO_4 itself. Within limits, the pH of these derivatives may be varied by changing the cation, and this property may have useful applications in buffering aqueous solutions.

ION-EXCHANGE PROPERTIES

Preliminary experiments established that alkali metal cations could be reversibly exchanged on the material and stripped with acid or salt solutions, and that the uptake of cations was accompanied by a decrease in pH due to liberation of H^+ ions. The amount of cation exchanged at equilibrium was a function of the weight of solid used and was independent of particle size; all these facts point to a mechanism involving ion exchange. Since considerably higher uptake is observed in alkaline solutions, the material must be a polyfunctional cation exchanger, with exchanging groups having differing acid strengths. Although we have no data at present on which to base a definite structure for the material, we may postulate that it consists of a

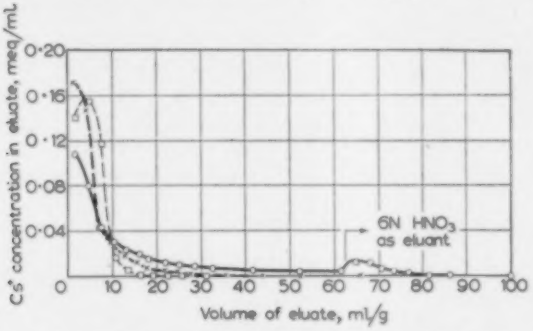

FIG. 5.—Elution of Cs^+ ion from zirconium phosphate with 3 N NH_4Cl solution.
Ordinates: Cs^+ concentration in eluate, mequiv/ml
Abscissae: ml eluate/g of exchanger
Legend: ⊙ 20°C.
× 56°C.
⊡ 82°C.

polymer network consisting of zirconium atoms linked together by bridging oxygen atoms, to which are attached acid phosphate groups having replaceable hydrogen atoms responsible for exchange; it is not known whether there may also be cross-linking provided by polyphosphate groups. The material is thus analogous to the organic cation exchange resins, with —Zr—O—Zr— units being equivalent to both the polymer chains and the cross-linking units of the latter, and acid phosphate groups replacing the sulphonic acid, carboxylic acid, or other functional groups. The new inorganic exchangers are thus gel exchangers similar to the organic resins, unlike the zeolites, which are crystal exchangers. In the absence of X-ray data we must look to analysis combined with capacity determinations and pH-titrations, over a range of compositions, to provide information on structure.

The equivalence between cation uptake and H^+ ion release was tested by equilibrating 0·5 g of exchanger with 5·0 ml of 0·015 N NaCl. Initial and final concentrations of sodium in solution were measured on an EEL flame photometer, and H^+ ion was estimated by titration with 0·0435 N NaOH, corrected for the blank value obtained on suspending 0·5 g of exchanger in distilled water. In two experiments 0·114 mequiv. of H^+ was released and 0·117 $\pm$ 0·007 mequiv. of Na^+ was exchanged. Attempts to obtain a similar balance in alkaline solution were unsuccessful, more hydroxyl ion being neutralized than could be accounted for solely by sodium ion exchange; there were indications of release of phosphate ion to solution in alkaline media, and this aspect requires further investigation.

When a solution of $CsNO_3$ (traced with ^{137}Cs) was passed down a column of zirconium phosphate, a typical breakthrough curve was obtained (Fig. 4); under suitable conditions the breakthrough is sharp, but the curve trails badly, and complete absorption is a slow process. Values of saturation capacity obtained by column runs, either to complete saturation or with linear extrapolation over the trailing part of the curve, are in good agreement with those determined by batch techniques (Table 2). Increasing the operating temperature sharpens the boundary but causes a greater degree of trailing, presumably due to increased hydrolysis of the caesium form at the higher temperature (see below). Most of the caesium may be rapidly removed with 3 N NH_4Cl (Fig. 5), although at room temperature the elution curve trails badly over the last 10 per cent of the capacity; this may be overcome by using a stronger eluant, e.g. 6 N HNO_3, or by eluting at a higher temperature. Mass balances based on activity determinations were good, as the following figures show:

Operating temperature	20°C	56°C
mequiv. Cs adsorbed/g	$1{\cdot}29_0$	$1{\cdot}22_2$
mequiv. removed by 3 N NH_4Cl	$1{\cdot}18_0$ (91·5%)	$1{\cdot}22_5$ (100·2%)
mequiv. removed by 6 N HNO_3	$0{\cdot}11_0$ (8·5%)	$0{\cdot}00_2$ (0·2%)
mequiv. remaining on column	$0{\cdot}00_2$ (0·2%)	$0{\cdot}00_1$ (0·1%)
mequiv. accounted for	$1{\cdot}29_2$ (100·2%)	$1{\cdot}22_8$ (100·5%)
Number of column volumes of eluant	80	40

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Exchange capacity as a function of conditions of preparation

Determination of equilibrium capacity as a function of pH shows the material to be a polyfunctional cation exchanger (Fig. 6), with appreciable capacity in acid solution and a total capacity in alkaline solution comparable on a weight basis with that of a typical cation exchange resin such as Zeo-Karb 225 or Dowex-50. On a volume basis the comparison is even more favourable because of density and swelling considerations; thus the capacity of zirconium phosphate is approximately 1, 3, and 5 mequiv/cm³ of wet settled exchanger in acid, neutral, and alkaline solutions respectively, compared with a value of ~2 mequiv/cm³ for the organic resins. The capacity varies continuously with pH in acid solution, reflecting the nature of the pH titration curve; capacities of individual batches vary appreciably, but all show the same type of pH dependence. Reduction of the ratio phosphate : zirconium causes an overall reduction in capacity, particularly in acid solution (Fig. 6); this supports the hypothesis that exchange occurs at sites on acid phosphate groups, and suggests that the most strongly dissociated phosphate groups are only produced from solutions containing excess phosphate. The temperature of drying has little effect on the capacity below pH 7 or at pH 12–13, but at temperatures above 50°C the loss of acidity over the region pH 7–12 is balanced by a decrease in capacity (Fig. 7); the almost complete recovery of capacity in the more alkaline solutions suggests that the non-exchanging condensed phosphate groups, although stable towards acid and neutral solutions, may be hydrolysed under mildly alkaline conditions to give exchanging groups. Since

TABLE 2.—EXCHANGE CAPACITY OF ZIRCONIUM PHOSPHATE PREPARATIONS

Sample	Capacity, mequiv/g	
	from neutral $CsNO_3$ solution	from CsOH solution, pH 12–13
I. Phosphate excess, prepared from $Zr(SO_4)_2$	0·67–0·75 (batch)	3·25, 3·21 (batch uptake) 3·29 (stripped with NH_4Cl)
II. Phosphate excess, prepared from $ZrOCl_2$	0·72, 0·75 (batch)	—
III. Phosphate excess, prepared from $ZrO(NO_3)_2$	1·28, 1·34, 1·35 (batch) 1·37, 1·35 (column)	4·44, 4·51 (batch) —
IV. Zirconium excess, prepared from $Zr(SO_4)_2$	0·21, 0·17 (batch)	—
Sample I after refluxing with water for 8 hr at 100°C.	0·68, 0·65 (batch)	—
Sample I after refluxing with conc. HNO_3 for 3 hr.	0·71, 0·72 (batch)	—

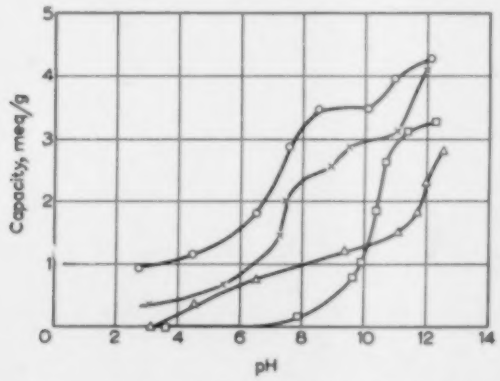

FIG. 6.—Cation exchange capacity of zirconium phosphate preparations of different PO_4/Zr ratio.
Ordinates: capacity, mequiv/g of exchanger dried at 30°C. Abscissae: pH.
Legend: as for Fig. 1.

material dried at the higher temperature is physically more stable in water at high temperatures, the maintenance of appreciable capacity is important.

Table 2 gives representative data obtained from both batch and column experiments on different samples of zirconium phosphate, using $CsNO_3$ solutions traced with ^{137}Cs. Examination of materials prepared with low ratios of phosphate to zirconium showed that they still contained anions representative of the original zirconium solution, and that these could be removed by treatment with chloride ion in acid solution, after which the chloride ion could itself be removed by stripping with nitric

acid. Furthermore, the anion exchange capacity so found was approximately equal to the content of the original anion found by analysis of the leachate from alkaline fusion of the original material (Table 3); nitrate was estimated volumetrically as NH_3 after reduction with Devarda's alloy, and sulphate gravimetrically as $BaSO_4$. After

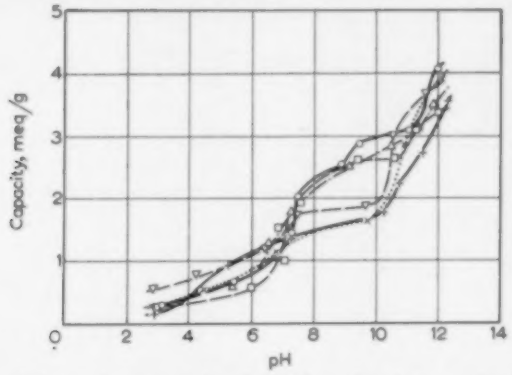

FIG. 7.—Cation exchange capacity of zirconium phosphate as a function of drying temperature.
Ordinates: capacity, mequiv/g referred to original weight at 30°C
Abscissae: pH
Legend: as for Fig. 2.

TABLE 3.—MIXED CATION–ANION EXCHANGERS BASED ON ZIRCONIUM PHOSPHATE

Material		Original anion (by analysis)	Chloride uptake in acid solution	Chloride removed by acid	Nitrate released by chloride ion
from nitrate	$PO_4 : Zr = 1{\cdot}4$	$NO_3 = 0{\cdot}03_5, 0{\cdot}01_7$ mequiv/g.	$0{\cdot}02_1, 0{\cdot}02_5$ mequiv/g.	$0{\cdot}02_3, 0{\cdot}01_9$	—
	$PO_4 : Zr = 0{\cdot}9$	0·06, 0·06	0·12, 0·10	0·11, 0·12	—
	$PO_4 : Zr = 0{\cdot}5$	0·75, 0·77	(a) 0·61, 0·61	0·63, 0·65	—
			(b) 0·59, 0·54	—	0·55, 0·53
$PO_4 : Zr = 0{\cdot}5$ (from sulphate)		$HSO_4^- = 0{\cdot}32$	0·30	—	—

equilibration with several batches of 0·1 N HCl, the chloride uptake was measured (a) from the decrease in chloride content of the equilibrating solutions, and (b) by stripping the washed chloride-form exchanger with dilute nitric acid. The agreement between exchange capacity and analytical results is quite good, considering the difficulty of accurately determining nitrate ion by this method at low concentrations. It would appear that when zirconium phosphate is precipitated without using excess phosphoric acid it may retain a certain amount of the anions originally associated with it, and that these may undergo reversible exchange with other anions. The proportion of such anions increases with decreasing phosphate : zirconium ratio, and is negligible in material prepared using excess phosphate; at low values of the ratio not all of the anions may be available for exchange (Table 3). Zirconium phosphate,

suitably prepared, may thus exhibit both cation- and anion-exchange properties simultaneously, and may find a use in removal of ionic impurities from solutions under suitable conditions.

Affinity series for alkali metal and alkaline earth ions

Table 4 gives values of mass distribution coefficients (K_D = mequiv/g of exchanger ÷ mequiv/ml of solution at equilibrium) for a number of ions in neutral solution on the hydrogen form of one batch of zirconium phosphate. As in the case of organic exchangers, K_D is seen to increase with decreasing concentration, while

TABLE 4.—MASS DISTRIBUTION COEFFICIENTS ON ZIRCONIUM PHOSPHATE (PHOSPHATE EXCESS)
Exchanger in hydrogen form equilibrated with neutral solutions at room temperature unless otherwise stated

Solution concentration	Li^+	Na^+	K^+	NH_4^+	Ag^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
0·001 N	—	200	—	—	—	—	~8000	—	—	—	—
0·010	—	—	—	—	98	—	—	—	126 (0·0092 N)	—	—
0·014	17	36 16 (100°C)	84	81	80	182 (0·013 N)	200 (0·013 N) 61 (100°C)	20	56	63 (0·012 N)	91
0·100	—	6	—	—	—	—	12	—	—	—	—

the affinity series for alkali metals and alkaline earths follow the pattern shown by many organic exchangers, viz.

$$Li < Na < K,NH_4 < Rb < Cs$$

$$Mg < Ca,Sr < Ba.$$

There are, however, differences between the behaviour of the organic and inorganic exchangers. Thus, when the uptake is plotted against the hydrated ion radius (values taken from JENNY[9] and PALLMAN[10]), although the alkaline earths and lower alkali metals give linear relationships similar to these found for the organic resins,[11] Cs and Rb appear to be selectively absorbed. The reason for this is not yet clear, although it might be due to a specific size effect. Another difference is the lower affinity of the inorganic exchanger for silver ions, with $K_D(Ag) \approx K_D(K)$; in both phenolsulphonic acid and sulphonated polystyrene resins $K_D(Ag) > K_D(Cs)$. Theoretical separation factors calculated from the relationship $\alpha_{M_1}^{M_2} = K_D(M_2)/K_D(M_1)$ suggest that in all these cases good separations could be achieved. Batch experiments with equimolar Cs–Rb mixtures and a preliminary determination of the Cs–Rb isotherm have shown that good separations are possible, and the material shows promise for alkali metal separations.

In alkaline solution, values of K_D were considerably higher, and the affinity series was less well marked; uptake of NH_4^+ ion was greatly reduced, presumably because of the weakness of the base NH_4OH, and a similarly low uptake was found for NH_4^+ ion from both neutral and alkaline solution on material which had been saturated

[9] H. JENNY *J. phys. Chem.* **36**, 2217 (1935).
[10] H. PALLMAN, *Soil Res. Berl.* **6**, 21 (1938).
[11] G. E. BOYD, J. SCHUBERT and A. W. ADAMSON *J. Amer. chem. Soc.* **69**, 2818 (1947).

with sodium ion from alkaline solution. Consequently, although all the alkali metals may readily be eluted with ammonium solutions from a column in acid form, it is extremely difficult to remove even sodium ion from a column in alkaline form by elution with ammonia solution.[12]

When values of K_D(Cs) as a function of acidity are plotted in the form of log K_D(Cs) vs. log (H^+) a straight line is obtained of slope (−1) (Fig. 8), as required for an ion-exchange equilibrium between two univalent species. Similar results have been reported by KRAUS,[4] who obtained straight lines with slopes of (−1/3) for the Ce^{3+}—H^+ exchange and (−1) for the Cs^+—NH_4^+ exchange.

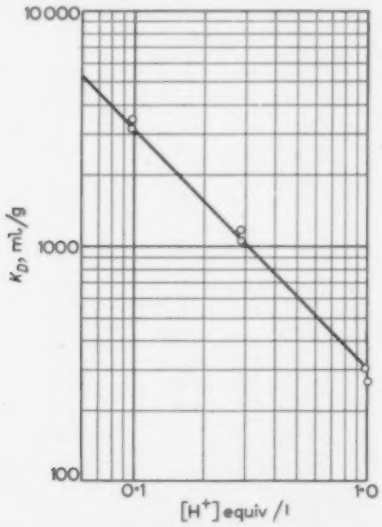

FIG. 8.—Mass distribution coefficient for Cs^+ ion on zirconium phosphate at different acidities.
Ordinates: K_D, ml/g. Abscissae: [H^+], equiv/l. [Cs^+] = 10^{-3} N.

The values of K_D given in Table 4 are seen to decrease with increasing temperature; when cation-substituted forms prepared by equilibration at room temperature are refluxed with water at 100°C, hydrolysis takes place and cations are released until a new equilibrium is set up, characterized by the lower distribution coefficient (Fig. 9). This hydrolysis is a consequence of the weakly acidic nature of the exchanger itself. Continued treatment with fresh batches of water produces progressive stripping; the extent of removal depends upon the affinity of the resin for the ion in question, removal of caesium being more difficult than that of sodium. It is possible in this way to remove sodium completely in several extractions from either the acid or alkaline forms; a useful consequence of the ready hydrolysis of sodium from the exchanger is the ease of removal of this ion from columns on which separations are being carried out, sodium beginning to appear even in the water washings after absorption. It may be feasible in some cases to remove sodium from a column simply by treatment with hot water; this would reduce the salt content of the regeneration effluent from the column.

[12] T. V. HEALY Private communication.

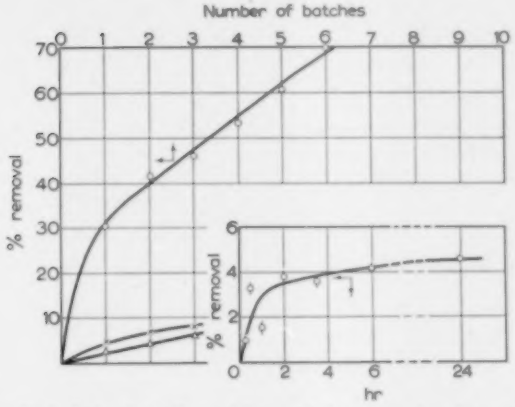

FIG. 9.—Hydrolysis of alkali metal forms of zirconium phosphate at 100°C.
Ordinates: percentage removal. Abscissae: no. of batches.
Legend: ⊙ Na^+.
△ Cs^+, from freshly-prepared exchanger.
× Cs^+, from acid-recycled exchanger.
Conditions: 0·3 g samples saturated with Cs or Na from neutral solution and then refluxed with 100 ml distilled water.
Inset: Removal of Cs^+ ion as a function of time.
Ordinates: percentage removal. Abscissae: hr.

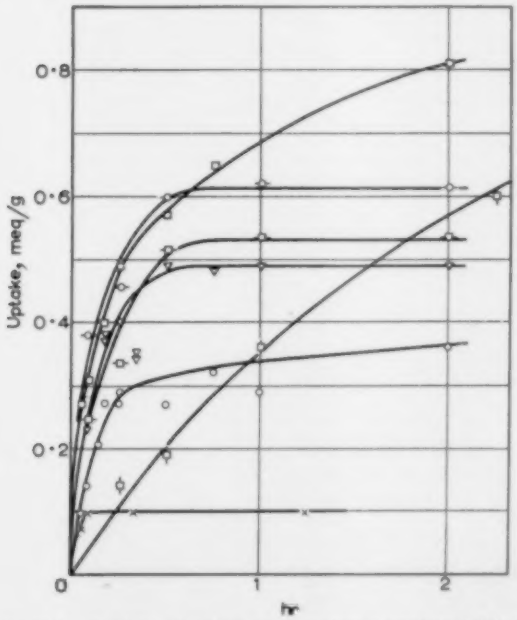

FIG. 10.—Rate of uptake of cations on zirconium phosphate (Mole Ratio 1·4 : 1).
Ordinates: uptake, mequiv/g. Abscissae: hr.
Legend:
⊡ 0·014 N Cs^+ on H-form, 20°C
–⊡– 0·014 N Cs^+ on H-form, 100°C
× 0·001 N Cs^+ on H-form, 20°C
} –80 + 100 B.S.S. mesh.

⊡ 0·014 N Cs^+ on Na-form, 20°C –60 + 80 B.S.S. mesh.

○ 0·014 N Nc^+ on H-form, 20°C
–⊙– 0·100 N Na^+ on H-form, 20°C
▽ 0·010 N Ag^+ on H-form, 20°C
} –80 + 100 B.S.S. mesh.

Rates of exchange of monovalent ions

Rate measurements with monovalent ions on the acid form of zirconium phosphate show the initial rate to be quite fast, followed by a slower uptake to equilibrium over a period dependent upon the conditions (Fig. 10). This result suggests a two-stage process involving a rapid surface uptake followed by a slower diffusion within the

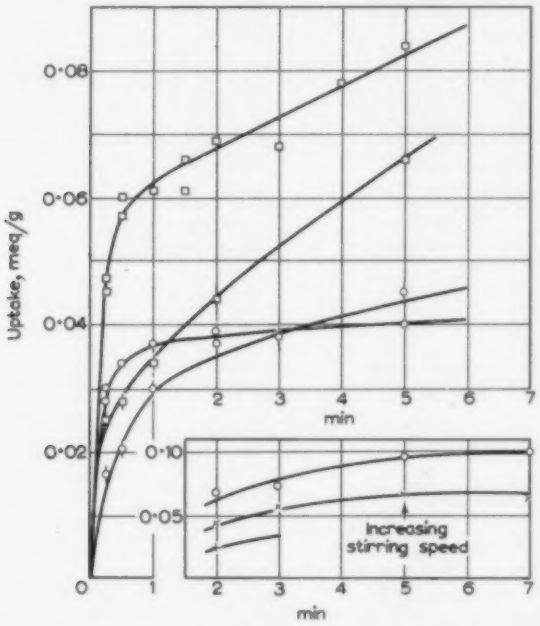

FIG. 11.—Initial rates from 0·001 N solutions on zirconium phosphate.
Ordinates: uptake, mequiv/g. Abscissae: min.
Legend: ⊡ Cs^+, −120 B.S.S. mesh exchanger
⊡ Cs^+, −60 + 80 B.S.S. mesh exchanger.
○ Na^+, −120 B.S.S. mesh exchanger.
○ Na^+, −60 + 80 B.S.S. mesh exchanger.
Inset: Effect of stirring rate.
Ordinates: uptake, mequiv/g
Abscissae: min

solid. There is a distinct correlation between initial rate and equilibrium distribution coefficient, both decreasing in the order $Cs^+ > Ag^+ > Na^+$ in this series. No significant increase in rate was observed at 100°C compared with 20°C, possibly because of the increased importance of the hydrolytic back-reaction. Measurements at short contact times (Fig. 11) show that in 10^{-3} N solutions the rate is dependent upon both stirring-rate and particle size, consistent with a rate-controlling step involving both film and particle diffusion, while in 10^{-2}–10^{-1} N solutions it is independent of stirring rate but dependent upon particle size, showing that in the more concentrated solutions solid diffusion is the rate-determining step. This behaviour

again parallels that of organic exchange resins.[11,13] The rate increases with increasing concentration, while the rate of caesium uptake on the sodium form is appreciably less than on the hydrogen form. Further work is required upon rates of exchange to clear up these points, but it is apparent from the curves given in Figs. 10 and 11 that the initial rates for zirconium phosphate compare favourably for those of organic resins. Higher rates could presumably be achieved if the degree of cross-linking could be reduced, but there is no convenient method of doing this at the moment, since cross-linking is not produced by controlling the proportion of an added reagent (viz. divinyl benzene in the case of organic resins), but arises adventitiously as a result of polymerization of the hydrolysed zirconium species in solution. The possibility of controlling the rates by incorporating other cations into the gel structure is receiving attention.

Acknowledgements—Our thanks are due to Dr. J. R. GROVER, of the Chemical Engineering Division, A.E.R.E., for preparing large batches of some of the material used in this work and to Mr. R. W. M. D'EYE for X-ray examination of the product.

[13] T. R. E. KRESSMAN and J. A. KITCHENER *Disc. Faraday Soc.* 7, 90 (1949); D. K. HALE and D. E. REICHENBERG *Ibid.* 7, 79 (1949).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 236 to 245. Pergamon Press Ltd., London

SYNTHETIC INORGANIC ION-EXCHANGE MATERIALS—II

HYDROUS ZIRCONIUM OXIDE AND OTHER OXIDES

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Abstract—The oxides ZrO_2, ThO_2, and TiO_2 behave as anion exchangers in acid and neutral solution and cation exchangers in alkaline solution, the pH at which their behaviour changes depending upon the oxide itself and possibly also upon the nature of the exchanging ion. The oxides have been prepared in granular form and their reversible reactions with ions in solution have been studied; they are monofunctional exchangers, with appreciable rates of exchange, and display the expected affinity towards ions in solution. Owing to their weakly basic nature, exchanged ions are readily removed by treatment with water. When ZrO_2 is treated with phosphoric acid it is converted into zirconium phosphate having properties qualitatively similar to the material described in Part I; the reaction cannot be solely one of anion exchange, but must involve breakdown of the oxide and introduction of further acid phosphate groups by neutralization.

WO_3 is a cation exchanger in acid solution, but dissolves in alkaline solution.

THE limitations to the use of organic ion-exchange resins have been discussed in Part I,[1] together with an account of the properties of the cation-exchange material zirconium phosphate. Relatively stable inorganic anion-exchange materials are found in nature, e.g. minerals in the apatite, sodalite, and cancrinite groups,[2] while anion exchange of fluoride for hydroxyl ion is also found in clays and soils to a limited extent.[3] However, the extent of exchange and the anions which may participate are frequently limited by crystallographic considerations. Anion exchange is also found in many insoluble hydrous oxides such as $Al(OH)_3$ and $Mg(OH)_2$,[4] in which fluoride and sulphate ions may exchange with hydroxyl ion. When prepared by alkaline precipitation from salt solutions, many hydroxides are found to contain varying amounts of adsorbed anions or cations according to the conditions of precipitation, and the absorbed ions may be displaced by washing with suitable salt solutions.[5] The electrokinetic properties of oxides suspended in different salt solutions have also been interpreted[6] in terms of surface hydroxyl groups capable of ionization and possessing ion-exchange properties. If we consider a surface hydroxyl group attached to a metal atom displaying amphoteric properties, then it is clear that ionization can take place in either of two ways, viz.

$$M-OH \rightleftharpoons M^+ + OH^- \quad (a)$$

$$M-OH \rightleftharpoons M-O^- + H^+ \quad (b)$$

[1] C. B. AMPHLETT, L. A. MCDONALD and M. J. REDMAN *J. inorg. nucl. Chem.* **6**, 220 (1958).
[2] R. H. S. ROBERTSON Private communication.
[3] S. MATTSON *Soil Sci.* **28**, 179 (1929); **30**, 459 (1930); **49**, 109 (1940); P. P. STOUT *Proc. Soil Sci. Soc. Amer.* **4**, 177 (1939).
[4] R. P. GRAHAM and A. E. HORNING *J. Amer. chem. Soc.* **69**, 1214 (1947); D. J. HISSINK *Trans. Faraday Soc.* **20**, 551 (1924); U. HOMAANN, K. ENDELL and D. WILM *Z. angew. Chem.* **47**, 2, 539 (1934).
[5] A. PINKUS and A. SALOMON *Bull. soc. chim. belg.* **47**, 844 (1938).
[6] P. J. ANDERSON *A.E.R.E. M/R*-2194 (1957); D. J. O'CONNOR *A.E.R.E. C/M*-230 (1955).

Case (a), which would be favoured by low pH, would lead to anion exchange, while at high pH, case (b) would lead to cation exchange. At the isoelectric point, where ionization would be at a minimum, we would expect virtually no exchange. The pH at which exchange is negligible will depend upon the values of the ionization constants K_a and K_b, which in turn will depend upon the chemical nature of M, and possibly also upon the nature of the exchanging anion or cation which is replacing OH^- or H^+ respectively. Thus, in the over-all exchange reaction

$$M - OH + X^- \overset{1}{\rightleftharpoons} M^+ + OH^- + X^- \overset{2}{\rightleftharpoons} MX + OH^-$$

if the affinity of M^+ for X^- is considerably greater than for OH^-, i.e. if K_2 is large, then even though the dissociation constant K_1 may be small the almost complete removal of M^+ in the second stage may suffice to overcome the normally low degree of ionization of MOH, and similarly for cation exchange. Consequently we may not find a well-defined pH at which the transition from cation to anion exchange takes place unless the affinities of the substrate for different ions are similar in magnitude.

Preliminary results have shown[7,8] that such amphoteric behaviour is exhibited by hydrous oxides such as zirconium oxide; the present paper deals in more detail with the oxides ZrO_2, ThO_2, TiO_2, and WO_3.

EXPERIMENTAL

Preparation of materials

The oxides ZrO_2, ThO_2, and TiO_2 were prepared by rapid addition of alkali to a well-stirred solution containing the appropriate salt, viz. $ZrO(NO_3)_2$ in 1 N HNO_3, $Th(NO_3)_4 \cdot 4H_2O$ in water, and $TiOSO_4$ in 1 N H_2SO_4; the last-named solution was prepared by fusing TiO_2 with potassium hydrogen sulphate and extracting the melt with hot 1 N acid. The dense flocculent precipitate of hydrous oxide was washed several times with water by decantation, filtered under suction, washed until free from salt and alkali, and dried at 50–100°C. On subsequent immersion in water the granular material broke down to a smaller particle size as in the case of zirconium phosphate,[1] after which it was stable to further treatment with water. Except in the case of ThO_2, which was of fine particle size, a range of mesh sizes was obtained, including coarse material of +20 B.S.S. mesh.

Tungsten trioxide was prepared in granular form by rapidly adding 35 ml of concentrated nitric acid to a well-stirred solution of 73 g $Na_2WO_4 \cdot 2H_2O$ in 250 ml of water. The dense yellow precipitate was filtered, washed, and dried at ~30°C to give a glassy, green, granular product after breakdown in water. A similar product is obtained by slow precipitation on slowly adding dilute acid to a tungstate solution; in this case a creamy-yellow gel is obtained, which may be washed and dried in the same manner.

pH-*Titrations*

These were carried out as described in Part I,[1] using solutions containing varying proportions of NaOH and NaCl for measurements in alkaline solution, and varying proportions of NaCl and HCl in acid solution; all solutions were initially 0·1 N in total Na^+ ion concentration. Sodium and chloride ion uptake from the equilibrating solutions were determined by photometry and by titration with standard silver nitrate solution.

Other properties

Exchange capacities, distribution coefficients, and rates of uptake were measured as described in Part I,[1] using chloride, bromide, iodide, sulphate, and chromate ions; the halide ions were determined by standard titration procedures, sulphate and chromate gravimetrically as the barium salts. Sodium exchange capacities were also measured, using flame photometry for analysis.

[7] K. A. Kraus and H. O. Phillips *J. Amer. chem. Soc.* **78**, 249 (1956).
[8] C. B. Amphlett, L. A. McDonald and M. J. Redman *Chem. & Ind. (Rev.)* 365 (1957).

PHYSICAL AND CHEMICAL PROPERTIES

The granular oxides are physically very stable in water and in aqueous salt solutions; the "basic" oxides ZrO_2, ThO_2, and TiO_2 dissolve in mildly acid solutions ($\geqslant$0·1 N) unless dried at elevated temperatures but are stable in alkaline solutions, while the converse is true for the "acidic" oxide WO_3. They are thus more limited in their range of application than the cation exchange materials based on insoluble salts such as the phosphates. When treated with water at 300°C, zirconium oxide undergoes little physical breakdown, and can under suitable conditions absorb corrosion-products from the metal vessel used for the test.

Table 1 shows that the pH of water in contact with the oxides is buffered to a

TABLE 1.—EQUILIBRIUM pH OF OXIDES IN AQUEOUS SUSPENSION

Oxide	Form	pH	Preparation
WO_3	H	2·85	$Na_2WO_4 + HNO_3$
TiO_2	(SO_4, OH)	3·35	$TiOSO_4 + NH_4OH$
ZrO_2	(ONa)	8·10	$Zr(SO_4)_2 + NaOH$
	(Cl, OH)	4·00	$ZrOCl_2 + NH_4OH$
ThO_2	(ONa)	9·80	$Th(NO_3)_4 + NaOH$

value dependent upon the chemical nature of the oxide, being more basic the more basic is the central metal, and also upon the form of the exchanger. Thus, zirconium oxide prepared using an excess of NaOH is largely in the (ONa) form, since at the high pH of the final suspension the material acts as a cation exchanger; as such it has an alkaline reaction, and analysis shows it to contain ~0·7 mequiv. sodium/g. If instead it is prepared by adding ammonium hydroxide to a solution of zirconyl chloride,* the final suspension is buffered to a pH of approximately 9, and under these conditions (see below) it behaves as an anion exchanger; consequently, the washed material is partly in the (OH) and partly in the (Cl) form, gives an acid reaction due to hydrolysis of the exchanged chloride ion, and is found to contain approximately 0·5 mequiv. Cl^-/g. The exact value of the chloride content varies with the amount of washing to which the material has been subjected; treatment of the (ONa) form with dilute acid gives, after washing, a product having the same reactions as that prepared from zirconyl chloride and ammonia.

pH-Titration of hydrous ZrO_2 shows it to be a monoacid base (Fig.1), and from the similarity in exchange properties ThO_2 would be expected to behave in the same manner. On ignition to constant weight at 1000°C, material originally dried at ~50°C lost ~24 per cent by weight, the residue on analysis agreeing with the formula ZrO_2. Hydrous tungsten trioxide lost 11 per cent by weight on ignition at 1000°C and gave a pH-titration curve which, though incomplete, suggested two stages of neutralization with a long buffer region before it dissolved completely in alkaline solution according to the reaction

$$WO_3(s) + 2\,OH^- \longrightarrow WO_4^{2-}(aq.) + H_2O.$$

* Supplied by F. W. Berk & Co. Ltd.

ION-EXCHANGE PROPERTIES

Anions are readily exchanged in neutral and acid solution upon the oxides ZrO_2, ThO_2, and TiO_2, while in alkaline solution (pH $\geqslant$ 11) cations such as Na^+ and Cs^+ are exchanged. Since chloride ion was used throughout for uptake determinations, early runs with ZrO_2 were confused by the fact that material prepared by precipitation with NH_4OH from solutions of $ZrOCl_2$ contains appreciable quantities of chloride. However, as shown by Table 2, when this is taken into account there is

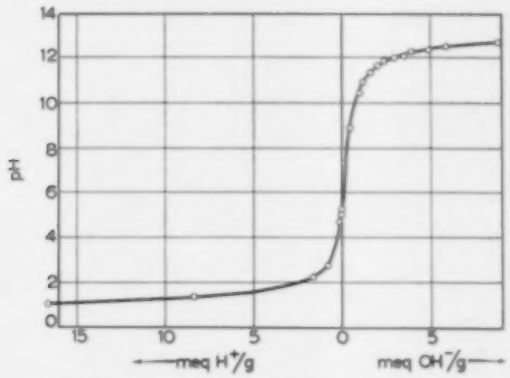

FIG. 1.—Titration curve for hydrous zirconium oxide gel.
Ordinates : pH
Abscissae : mequiv. OH^-/g (to the right of O)
mequiv. H^+/g (to the left of O)
Conditions : 0·5 g equilibrated with 75 ml of 0·1 N (NaOH + NaCl) or of 0·1 N (HCl + NaCl).

good agreement between different batches of material, the capacity in acid solution being ~1–1·2 mequiv/g, while in neutral solutions it is appreciably lower. Furthermore, the sum of the chloride found on analysis and the capacity found for unstripped material is approximately equal to the total capacity determined on stripped material. Variations in both chloride content and chloride capacity of unstripped material are probably due to varying removal of chloride by hydrolysis during washing in the final stages of preparation (see below). Capacities quoted in Table 2 were usually determined on material dried at 100°C, but figures obtained for material dried at 30° and at 100° relative to the original weight at 30°C show that there is a slight decrease in capacity (~9 per cent) on drying at 100°C. It is also interesting to note that the weight loss at 100°C for the nitrate form prepared by stripping with sodium nitrate is approximately twice that for the mixed chloride–hydroxide form obtained in the original preparation (19·6 per cent and 10·0 per cent respectively).

Attempts to measure the balance between chloride ion absorbed and hydroxyl or other anion released were frustrated by the measurable solubility of ZrO_2 in dilute acid, and also by the difficulty of preparing the material in a form containing only one replacable anion. Thus, if we attempt to prepare the nitrate form by stripping with $NaNO_3$, it is partly hydrolysed in water to give a mixed hydroxyl-nitrate form. The most promising approach appears to be to prepare the hydroxyl form if possible by complete stripping with water of either a suitable anionic form or of a cationic form.

The dependence of capacity upon pH was measured for both ZrO_2 and ThO_2,

TABLE 2.—UPTAKE OF CHLORIDE ION BY HYDROUS ZIRCONIUM OXIDE

Sample	Saturation capacity, mequiv. Cl^-/g		mequiv. Cl^-/g removed by NO_3^- ion	Original Cl^- content by difference
	from 0·1 N HCl	from 0·1 N NaCl		
(ONa) *form*	0·94	—	—	—
(OH, Cl) *form*				
Berks W1	—	0·15	—	—
Berks W2	0·76	—	—	—
Berks W3	0·56, 0·59	0·15, 0·20	—	0·47, 0·58
(NO_3) *form*				
Berks W1	1·15, 1·14 (uptake) 1·16, 1·16 (stripping)	—	0·62, 0·56	—
Berks W3	1·05, 1·00, 1·05	0·75	0·49, 0·54	0·47, 0·58
Berks W3, after chloride uptake and water stripping	0·99, 0·97	—	—	—
Berks W3, dried at room temperature	1·02, 1·02	—	—	—
Berks W3, dried at 100°C	(a) 1·16, 1·16 re weight at 100°C (b) 0·93, 0·93 re original weight	—	—	—

with the results shown in Fig. 2; weighed amounts of exchanger were equilibrated with successive batches of 1 N NaCl solution containing varying concentrations of NaOH or of HCl until saturation was reached. The pH was measured and the solid filtered and washed, after which it was stripped with dilute acid and analysed for sodium and for chloride. Fig. 2 shows also values for single determinations of caesium capacity and for single batch uptakes of chloride ion. Both anion and cation exchanger capacities are monotonous functions of pH, in agreement with the simple titration curve in Fig. 1. The chloride anion capacity decreases with increasing pH; this is probably due largely to suppression of the ionization of surface hydroxyl

groups, since except at relatively high pH the ratio of Cl^- to OH^- ions will always be large. At pH $\sim$ 11, anion exchange capacity becomes negligible, and above this value the cation exchange capacity increases with increasing pH. Zirconium and and thorium oxides, while showing similar qualitative behaviour, differ in the pH at which the alteration from anion-exchange to cation-exchange is observed, this being lower for ThO_2. On the basis of bulk chemical properties we would expect the reverse to be true, and we must conclude either that the surface properties do not completely parallel the bulk properties, or that other factors enter into the situation,

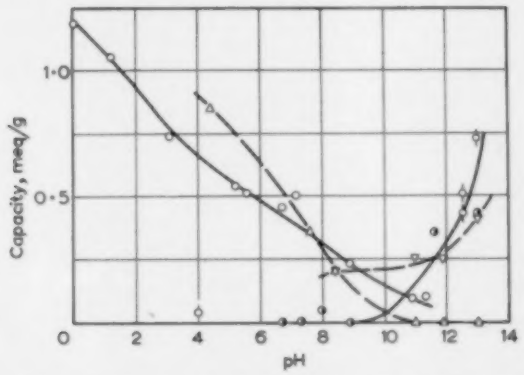

FIG. 2—Anion and cation exchange capacity of ZrO_2 and ThO_2.
Ordinates : capacity, mequiv/g
Abscissae : pH
Legend : ○ ZrO_2, chloride ion capacity.
◑ ZrO_2, sodium ion capacity.
○ ZrO_2, caesium ion capacity.
△ ThO_2, chloride ion capacity.
▽ ThO_2, sodium ion capacity.

as discussed in the introduction of this paper; it would be interesting to develop this work further, using different exchanging ions.

Detailed investigations were not carried out on either tungsten or titanium oxides, since their capacities were found to be low. Titanium oxide had a capacity of $\sim$0·2 mequiv/g for chloride ion in acid solution, while the cation-exchange capacity of tungsten oxide was between 0·32 and 0·36 mequiv/g over the range of pH 3–6, falling rapidly to zero at higher pH values.

Values of mass distribution coefficients for some anions on ZrO_2 and TiO_2 and for alkali metal cations on ZrO_2 in alkaline solution are given in Table 3; these show the expected affinity relationships, with chloride ion being more strongly adsorbed than either bromide or iodide ion. However, the differences between the anions are less marked than those between the cations and very much less so than for cations on zirconium phosphate;[1] in fairly concentrated solutions sulphate ion is much less strongly adsorbed than the others, while chromate ion is rapidly adsorbed to an equilibrium value comparable with that of the monovalent anions. As expected, anion distribution coefficients increase with decreasing concentration and decrease as the pH is raised.

When substituted anionic forms of ZrO_2 are washed with water, hydrolysis takes place and a large proportion of the anion may be released to solution, particularly

at elevated temperatures; it is therefore impossible to wash them completely free of traces of adhering solution, e.g. the washings from the chromate form are always yellow. The iodide form, which is colourless or white, turns yellowish-brown on standing in air, due to oxidation of the liberated iodide ion, and the iodine so formed may be extracted into organic solvents. Measurements of the release of chloride or iodide ion by hydrolysis show (Fig. 3) that 40–50 per cent may be removed in one

TABLE 3.—DISTRIBUTION COEFFICIENTS ON HYDROUS ZrO_2 AND TiO_2
Single batch equilibration of 0·2 g exchanger with 20 ml of solution

Ion	Solution	K_D, ml/g	
		ZrO_2	TiO_2
Cl^-	0·1 N HCl	11·0 (a) 10·0 (b), (d) 9·3 (c)	2·8
	0·01 N HCl	80·0 (c)	—
	0·1 N NaCl	7·2 (c)	1·1
	0·01 N NaCl	—	1·2
Br^-	0·1 N KBr	5·6 (c)	—
I^-	0·1 N KI	5·5 (c)	1·2
CrO_4^{2-}	0·1 M K_2CrO_4	5·5 (c)	—
SO_4^{2-}	0·1 M Na_2SO_4	~1 (c)	—
Na^+	0·045 M MOH	2·9 (c)	—
K^+		3·8	
NH_4^+		0·4	
Cs^+		9·7	

(a) (OH) form, prepared by exhaustive stripping of (Cl) form with hot water.
(b) Berks W1, (NO_3) form, prepared by stripping with HNO_3 until free of chloride.
(c) Berks W3, (NO_3) form, prepared by stripping with HNO_3 until free of chloride.
(d) (ONa) form, prepared from $Zr(SO_4)_2$ and NaOH.

stage by refluxing at 100°C, and that on repeated batch treatment practically the whole of the halide may be removed, presumably with replacement by hydroxyl ion; iodide is removed more readily than chloride, as would be expected. This method, which may enable the hydroxide form of the exchanger to be prepared, is analogous to the regeneration of the weak base anion-exchanger resin Amberlite IR-4B by treatment with water.[9] Preliminary results (Table 2) suggest that the exchange capacity of material stripped in this way is appreciably lower than that of fresh material, while the leaching is unaffected by drying at 100°C in the chloride form. Since leaching was studied from mixed (X, NO_3) forms prepared by equilibration of nitrate stripped material with either chloride or iodide solutions ($X \equiv Cl^-, I^-$), care has to be taken to use materials equilibrated to the same extent with the ion X^- if

[9] H. P. KORTSCHAK and J. H. PAYNE *J. Amer. chem. Soc.* **70**, 3139 (1948).

results are to be comparable with each other. In the case of (I, NO_3) forms containing a low proportion of iodide the percentage removal of iodide is much higher than in completely equilibrated material, suggesting that iodide is more readily removed than nitrate by hydrolysis; experiments with mixed (Cl, NO_3) forms and with the fully saturated (Cl) form suggest that chloride and nitrate behave similarly to each

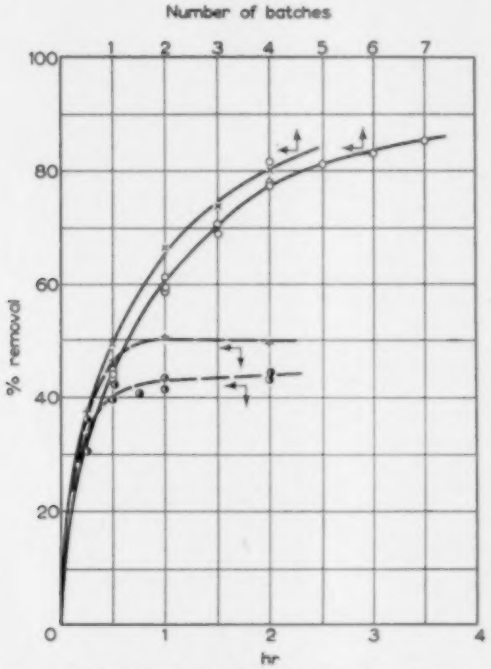

FIG. 3.—Hydrolysis of chloride and iodide forms of ZrO_2 at 100°C.
Ordinates : percentage removal
Abscissae : hr (at foot of diagram)
no. of batches (above diagram)
Legend : ⊙ Chloride removal in successive batches (upper scale).
◑ Chloride removal in single batch (lower scale).
× Iodide removal in successive batches (upper scale).
+ Iodide removal in single batch (lower scale).

other. We may thus draw up the following rough affinity series in 0·1 N solution:

$$Cl^-, NO_3^- > Br^-, I^-, CrO_4^{2-} \gg SO_4^{2-}.$$

Rate measurements (Fig. 4) for chloride, bromide, and iodide uptake show that uptake is initially rapid; exchange is almost complete within 30 sec from 0·1 N solution using fine material (~100 B.S.S. mesh). The initial rate increases with increasing concentration and with decreasing particle size; it appears to be independent of pH, but is less for material which has been stripped with hot water, and is less for iodide ion than for either chloride or bromide.

CONVERSION OF ZIRCONIUM OXIDE TO ZIRCONIUM PHOSPHATE

When the oxide is treated with phosphoric acid it is converted to the phosphate, and assumes cation-exchange properties. Titration curves (Fig. 5) show that the

product is qualitatively similar to that prepared by direct precipitation from zirconium salt solutions; the acidity of the product, and also its capacity (Fig. 6), are dependent upon the concentration of phosphoric acid used in its preparation. Owing to the insolubility of the product, this cannot be due to equilibrium considerations; since

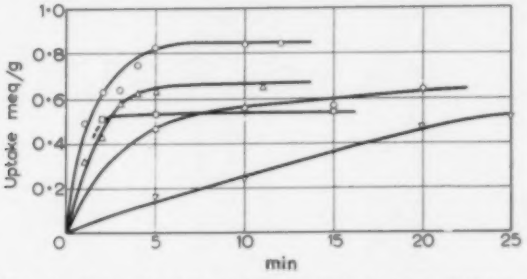

FIG. 4.—Rates of uptake on hydrous ZrO_2 (−20 + 40 B.S.S. mesh).
Ordinates : uptake, mequiv/g
Abscissae : min
Legend : ⊙ Chloride ion from 0·1 N HCl.
⊙ Chloride ion from 0·01 N HCl.
△ Chloride ion from 0·1 N NaCl.
⊡ Bromide ion from 0·1 N KBr.
▽ Iodide ion from 0·1 N KI.

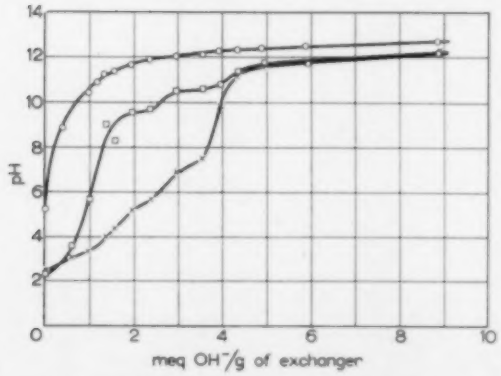

FIG. 5.—Titration curves for products of reaction between zirconium oxide and phosphoric acid
Ordinates : pH
Abscissae : mequiv. OH^-/g
Legend : ⊙ Hydrous ZrO_2 gel.
⊡ ZrO_2 treated with 0·3 M H_3PO_4.
× ZrO_2 treated with 16 M H_3PO_4.

however, granular zirconium oxide is appreciably broken down in strong phosphoric acid solutions it is probably due to the uptake of more phosphate than corresponds to the anion-exchange capacity, by neutralization of basic groups released during the physical breakdown. This hypothesis is supported by a comparison of the cation exchange capacity of the product with the anion exchange capacity of the starting material. With a capacity of ~1·2 mequiv/g in acid solution we would expect to observe the absorption of 1·2 mmole/g of $H_2PO_4^-$ ion or 0·6 mmole/g of HPO_4^{2-} ion if no breakdown occurred and the mechanism were solely the replacement of OH^- or Cl^- ion by acid phosphate ion. If all the hydrogen atoms in the product were

available for exchange the product would have a total cation exchange capacity lying between 2·4 and 0·6 mequiv/g, depending on the proportions of the different acid phosphate groups. Since the observed values in alkaline solution are considerably in excess of the higher of these figures we conclude that in phosphoric acid solution there is appreciable breakdown, followed by the introduction of further phosphate

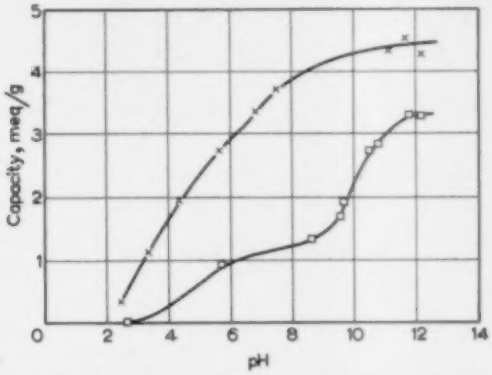

FIG. 6.—Capacity of zirconium phosphate prepared from ZrO_2 and phosphoric acid.
Ordinates : cation-exchange capacity, mequiv/g.
Abscissae : pH.
Legend : ⊡ / × as for Fig. 5.

groups by neutralization reactions. It is intended to investigate further the properties of zirconium phosphate prepared from zirconium oxide using different concentrations of phosphoric acid and of soluble phosphates, since this may offer a more convenient method of varying the properties of the product (in particular the degree of cross-linking) than direct precipitation; in addition it may provide a cheaper method of manufacture. Preliminary rate measurements have shown that the uptake of silver ion is slower than for the materials described in Part 1,[1] and the distribution coefficient is smaller ($K_D = 80$ for directly precipitated material, 48 for material prepared via the oxide, both from 0·01 N $AgNO_3$ solutions); the decreased specificity might indicate a smaller degree of cross-linking, although this would lead to an increase in rate, other factors being equal.

Acknowledgement—We wish to thank F. W. Berk & Co. Ltd., for supplying some samples of granular zirconium oxide used in this work.

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 246 to 251. Pergamon Press Ltd., London

THE INTERACTION OF AMMONIUM AND POTASSIUM HEXABROMOÖSMATE(IV) AND LIQUID AMMONIA AT 25°C—II

THE AMMONIA-SOLUBLE PRODUCTS*

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Abstract—The ammonia-soluble product of the reaction between K_2OsBr_6 and liquid ammonia at or near 25°C is shown to consist of diamagnetic μ-nitridobis-[dibromotetrammineosmium(IV)] bromide which was isolated as the 3-hydrate, and converted to the corresponding iodide. The same product is formed when $(NH_4)_2OsBr_6$ is used in the presence of NH_4Br, but at the same time paramagnetic and ammonia-soluble hexammineosmium(III) bromide is produced; formation of the latter is attributed to a reaction between ammonium bromide and the ammonia-insoluble product, i.e. hexammineosmium(III) hexabromoösmate(III).

IT has been shown previously[1] that essentially one-half of the osmium as ammonium hexabromoösmate(IV) that reacts with liquid ammonia at or near room temperature appears as an ammonia-insoluble solid that consists of hexammineosmium(III) hexabromoösmate(III). The present paper is concerned with the separation, identification, and certain reactions of the substances that comprise the ammonia-soluble reaction products.

EXPERIMENTAL

Unless otherwise indicated, all materials, analytical procedures, and experimental methods were the same as those described previously.[1, 2] Upon completion of the reaction between ammonium or potassium hexabromoösmate(IV) and liquid ammonia at or near room temperature, the combined filtrate and washings from the separation of the ammonia-insoluble product was evaporated to provide a solid residue consisting of a mixture of yellow-tan and white crystals.‡ These solids were treated as follows.

In a typical case (Run 8, Table 1), 0·65 g of the solid mixture was ground to a fine powder and treated with 300 ml of absolute alcohol to remove KBr and NH_4Br. The resulting suspension was stirred occasionally over a period of 3 days at 30°C, the colourless supernatant solution was decanted, and the alcohol extraction was repeated for 1 day. The *odourless* microcrystalline yellow-tan solid was filtered, washed with alcohol until the washings failed to give a positive test for bromide ion, dried under reduced pressure, and finally over anhydrous magnesium perchlorate. The combined

* This work was supported in part by The Atomic Energy Commission, Contract AT-(40-1)-1639.
† Present address: Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pa.
‡ The crude solid products had a peculiar odour; inhalation of the vapour caused headache and nausea.
[1] G. W. WATT and L. VASKA *J. inorg. nucl. Chem.* **5**, 304 (1958).
[2] G. W. WATT and L. VASKA *J. inorg. nucl. Chem.* **5**, 308 (1958).

filtrate and washings was found to contain only traces of osmium; evaporation to dryness yielded a white crystalline solid. Found: K, 21·2; Br, 72·2; NH_4^+, 6·55; these data correspond to a KBr : NH_4Br ratio of 8 : 5 (see Discussion). Analytical data for representative alcohol-insoluble products are given in Table 1, together with certain other data pertaining to the initial reactions with ammonia; these latter data are included, since they bear upon the identity of the ammonia-soluble products.

TABLE 1.—DATA RELATING TO AMMONIA-SOLUBLE PRODUCTS

Run No.	Starting material	Initial concentrations, mole/l.*		Product†		
		$(OsBr_6)^{2-}$	NH_4^+	Os %	Br %	Os:Br
8	K_2OsBr_6	0·036	0	38·2	40·5	1:2·52
6	K_2OsBr_6	0·069	0	38·5	—	—
10A	$(NH_4)_2OsBr_6$	0·041	0·08	38·5	39·7	1:2·46
23A	$(NH_4)_2OsBr_6$ $+NH_4Br$	0·157	0·80	38·6	40·7	1:2·51

* i.e. In the initial reactions between bromoösmate(IV) and liquid ammonia at or near 25°C.
† Calc. for $[Os_2(NH_2)_3NBr_2]\ Br_2 \cdot 3H_2O$: Os, 38·6; Br, 40·6; Os : Br, 1 : 2·50.

For the total products of the initial reactions, material balance data are significant. Thus, for Run No. 8, the yields based on bromine used as K_2OsBr_6 are as follows: ammonia-insoluble product, 22 per cent; alcohol-insoluble fraction of the ammonia-soluble product, 21 per cent; alcohol-soluble fraction of the ammonia-soluble product, 56 per cent; total accounted for, 99 per cent. Similarly, the yields based on osmium are: ammonia-insoluble product, 48 per cent; ammonia-soluble (and alcohol-insoluble) product, 50 per cent; total, 98 per cent.

The data given in Table 1 suggest that the ammonia-soluble product consists of μ-nitridobis-[dibromotetrammineosmium(IV)] bromide, i.e. a binuclear complex strictly analogous to the corresponding chloride described by DWYER and HOGARTH.[3] All of the results of the present studies support this interpretation for those cases in which K_2OsBr_6 was used in the initial reactions with liquid ammonia. Otherwise, the analytical data given in Table 1 are misleading. The structure proposed by DWYER and HOGARTH,[3] suggests that the binuclear chloride complex should be diamagnetic; the pure bromide prepared in the present work was diamagnetic. However, when $(NH_4)_2OsBr_6$ was used in the initial reaction with liquid ammonia, and more particularly when the reaction was carried out in the presence of added ammonium bromide, the alcohol-insoluble fraction of the ammonia-soluble reaction product was found to be paramagnetic. For example, the magnetic susceptibility per gramme of product from Run 23A ($\chi_g \times 10^6$) was 0·8. Thus, the analytical data for the product do not reflect the presence of a paramagnetic species in the product that otherwise consists principally of the binuclear complex. Accordingly, the remainder of the experiments

[3] F. P. DWYER and J. W. HOGARTH *J. roy. Soc. N.S.W.* **84**, 117 (1951).

described in this paper are concerned with efforts to separate and identify the components of the gross ammonia-soluble product.

Purification by extraction with liquid ammonia at $-75°$

Anhydrous liquid ammonia (5 ml) was condensed at $-75°$ on about 1 g of the 3-hydrate of the ammonia-soluble product that had been freed of ammonium bromide in the manner described above. The resulting brown solution was removed by filtration and the solid residue was washed twice at $-75°$ with 5 ml portions of ammonia to provide 0·25 g of the purified binuclear complex. Found: Os, 38·7; Br, 40·5. Calc. for $[Os_2(NH_3)_8NBr_2]Br_3 \cdot 3H_2O$: Os, 38·6; Br, 40·6. A sample of this product was converted to the iodide by dissolving it in the minimum quantity of water and adding an excess of hydriodic acid. The pale yellow precipitate was filtered, washed with water, and dried over $Mg(ClO_4)_2$. Found: Os, 34·1. Calc. for $[Os_2(NH_3)_8NBr_2]\ I_3 \cdot 3H_2O$: 33·8.

A detailed examination of the residue obtained by evaporating the solvent from the combined supernatant solution and washings from the preceding separation failed to yield conclusive results. Treatment of this residue with hot concentrated hydrobromic acid followed by fractional crystallization from water, alcohol, and acetone mixtures gave small fractions of osmium-containing solids that exhibited a wide variety of elemental compositions and colours; these apparently consisted of mixtures.[4] The isolation of a brown solid having an osmium content of 81·2 per cent is suggestive of extensive ammonolysis.

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Identification of hexammineosmium(III) *ion*

After removal of ammonium bromide as described above, ca. 1·5 g of the product from Run 23A was subjected to fractionation from dilute hydrobromic acid and alcohol at or near room temperature in a manner similar to that referred to above, but too detailed for inclusion here.[4] Thus, nine separate fractions were obtained; the four least-soluble products were diamagnetic and the analytical data suggested that they consisted principally of the binuclear complex. Found: (Os : Br, 1 : 2·36 to 1 : 2·41). The five more-soluble fractions consisted of paramagnetic solids, and the presence of hexammineosmium(III) bromide as a component of these mixtures was established by means of both X-ray diffraction patterns and magnetic susceptibility data. Although the pure hexammine bromide was not obtained in any case, purification was accomplished by conversion to the corresponding iodide. Thus, 0·1 g of the pale green solid was dissolved in 5 ml of water, a trace of insoluble solid was removed by filtration and rejected, and 10 ml of a saturated solution of sodium iodide in absolute alcohol was added to the filtrate. The resulting light green precipitate was redissolved in water, treated again with sodium iodide in alcohol, and the resulting yellow solid was filtered, washed with water and alcohol, and dried over $Mg(ClO_4)_2$. Found: N, 12·7; μ, 2·2 B.M. Calc. for $[Os(NH_3)_6]\ I_3$: N, 12·5. This product gave an X-ray diffraction pattern identical with that reported earlier.[1]

Further purification of μ*-nitridobis-*[*dibromotetrammineosmium*(IV)] *bromide*

The crude ammonia-soluble and paramagnetic solid product (3·5 g) from Run 18A[4] was treated with 10 ml of water to provide a brown solid and an orange-coloured

[4] For further details see: L. VASKA Dissertation, The University of Texas, 1956.

solution. Following filtration, 30 ml of ethyl alcohol was added to the orange-coloured filtrate, the mixture was cooled to 0°C, and the resulting tan diamagnetic solid was filtered, washed with alcohol, and dried as described above. Found: Os, 39·2; Br, 40·6; N, 12·8. Calc. for $[Os_2(NH_3)_8NBr_2]\,Br_3{\cdot}3H_2O$: Os, 38·6; Br, 40·6; N, 12·8. The brown solid was treated with an additional 20 ml of water, but only a small part dissolved to form an intensely brown solution. After filtration, the brown solution was treated with a few drops of 48 per cent HBr followed by 60 ml of ethyl alcohol. After cooling to 0°C, the tan diamagnetic solid was separated and dried as described above. Found: Os, 38·9; Br, 40·3. Calc. for $[Os_2(NH_3)_8NBr_2]\,Br_3{\cdot}3H_2O$: Os, 38·6; Br, 40·6. X-ray diffraction data are given in Table 2.

TABLE 2.—X-RAY DIFFRACTION DATA FOR $[Os_2(NH_3)_8NBr_2]Br_2{\cdot}3H_2O$

d (Å)	I/I_0	d (Å)	I/I_0
6·8	1·0	3·32	0·9
3·80	0·6	2·70	0·5
3·67	0·6	2·11	0·9

This process of fractional dissolution was continued by use of hot hydrobromic acid in varying concentrations to provide solutions from which several fractions of solid products were isolated as described above. These solids were diamagnetic, or nearly so, and their composition as determined by analysis corresponded rather closely to that of the binuclear complex, e.g. Os : Br = 1 : 2·44, 1 : 2·55. The conductivities of aqueous solutions of several of these products were measured and were found to be higher than expected for an electrolyte of the type represented by the binuclear complex (i.e. of the order of 500 mhos mole^{-1} for 10^{-3}–10^{-4} M solutions). Moreover, the conductivities of these solutions increased rapidly with time; this is indicative of extensive hydrolysis and is consistent with previous observations on an analogous compound.[3]

DISCUSSION

The foregoing data show that, when K_2OsBr_6 reacts with liquid ammonia at or near 25°C, the ammonia-soluble product which accounts for one-half of the osmium used consists of essentially pure diamagnetic μ-nitridobis-[dibromotetrammineosmium(IV)] bromide, which was isolated as the 3-hydrate. When, however, $(NH_4)_2OsBr_6$ is employed in the reaction at 25°C, paramagnetic hexammineosmium (III) bromide is a component of the ammonia-soluble product. Formation of this latter species is favoured when the initial reaction is carried out at still higher ammonium ion concentrations provided by addition of ammonium bromide.

After isolation of the binuclear complex as the 3-hydrate, purification was accomplished by extraction with liquid ammonia even though this product was obtained from an ammonia solution at −33·5°C. This is possible owing to the lower temperature at which the 3-hydrate was extracted (−75°C), the low solvent to solid ratio employed, and the apparently lower solubility and/or rate of solution of the 3-hydrate as compared with the anhydrous salt. Qualitative evidence for ammonolysis at −75°C

is attributable to the absence of any appreciable concentration of ammonium ion which was present in the initial exposure to ammonia at −33·5°C and hence suppressed solvolytic reactions. In addition to the purification accomplished by treatment with liquid ammonia, a product of high purity was also obtained by recrystallization from water.

That the brown ammonia-soluble product is the bromine analogue of the chloro complex described by DWYER and HOGARTH[3] is strongly supported by the similarity of mode of formation, colour, an osmium : bromine ratio of 2 : 5, and the demonstration of the presence of three ionic bromines (as evidenced by conversion to the tri-iodide). Furthermore, the fact that the bromide proved to be diamagnetic lends support to DWYER and HOGARTH's assumption of a 4^+ oxidation state of osmium and and their proposed structure,

$$\left[\begin{array}{cccc} NH_3 & NH_3 & NH_3 & NH_3 \\ \diagdown & \diagup & \diagdown & \diagup \\ X\text{—}Os\text{—} & & N = & Os\text{—}X \\ \diagup & \diagdown & \diagup & \diagdown \\ NH_3 & NH_3 & NH_3 & NH_3 \end{array}\right] X_3$$

With the possible exception of the carbonyl, $Os_2(CO)_9$, which appears to involve Os—Os bonds,[5] polynuclear complexes of osmium other than the type under discussion have not been reported previously. The recent work of MATHIESON, MELLOR and STEPHENSON[6] however, has shown that the hydroxopentachlororuthenate(IV), $K_2[Ru(OH)Cl_5]$ is actually a monohydrate of the dimer, $[(Cl_5Ru\text{—}O\text{—}RuCl_5)_2]^{4-}$; this species is diamagnetic, in contrast to the usual experience with Ru(IV) compounds. This case supports our assumption that, in the binuclear osmium complex, coupling of electron spins of the two paramagnetic osmium(IV) atoms is feasible in the arrangement —Os—N=Os— and renders this group diamagnetic.

The presence of paramagnetic hexammineosmium(III) bromide in the ammonia-soluble product from runs in which $(NH_4)_2OsBr_6$ was used is understandable on the basis of results reported earlier.[1] It seems indicated that the hexammine bromide results from the reaction between ammonium bromide and the *ammonia-insoluble* product, i.e. hexammineosmium(III) hexabromoösmate(III). This is supported by the observation that, when the initial reactions at 25°C were carried out in the presence of added ammonium bromide and hexammineosmium(III) bromide was found among the ammonia-soluble reaction products, the yields of ammonia-insoluble product were relatively low, i.e. they fell somewhat short of accounting for one-half of the osmium used in the initial reactions. We do not wish to imply, however, that the paramagnetism exhibited by the crude ammonia-soluble product is wholly attributable to the hexammine bromide. Fractionation of a number of these products led to the isolation of several impure paramagnetic solids that exhibited strikingly different colours probably caused by the presence of other osmium complexes in quantities too small to permit isolation as pure compounds.

With respect to the over-all reaction between bromoösmate(IV) and liquid ammonia at 25°C, only the fate of the solvent molecules that are oxidized prevents representation of the stoicheiometry involved. If, for example, it is assumed that

[5] N. V. SIDGWICK *The Chemical Elements and Their Compounds* p. 1509. Oxford University Press (1951).
[6] A. McL. MATHIESON, D. P. MELLOR and N. C. STEPHENSON *Acta Cryst.* **5**, 185 (1952).

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ammonia is oxidized to hydrazine that was not detected because it was co-ordinated with Os^{3+} and/or Os^{4+}, we may write,

$$4K_2OsBr_6 + 22NH_3 \rightarrow$$
$$[Os(NH_3)_6](OsBr_6) + [Os_2(NH_3)_8NBr_2]Br_3 + 8KBr + N_2H_4 + 5NH_4Br$$

for the principal reaction. When K_2OsBr_6 is used as the starting material, the two osmium-containing products are found in essentially a 1 : 1 ratio, while, as shown above, the ratio of KBr to NH_4Br found is 8 : 5.

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THE PROPERTIES OF INORGANIC COMPOUNDS IN ORGANIC SOLVENTS—I

THE HYDROLYSIS AND POLYMERIZATION OF QUADRIVALENT PLUTONIUM NITRATE SPECIES IN DIETHYLENE GLYCOL DIBUTYL ETHER

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(*Received* 14 *October* 1957)

Abstract—Colour changes in weak acid solutions of plutonium (IV) nitrate in diethylene glycol dibutyl ether have been shown to be due to hydrolysis, and subsequent formation of a polymeric form of plutonium (IV), which shows many correspondences with the colloid formed in aqueous solution. The polymer appears to be fairly stable in this solvent at room temperature but on heating the solution, a precipitate is formed; X-ray analysis shows that this is a hydrated plutonium dioxide. A possible reaction scheme for the formation of the polymer is discussed.

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THERE are a number of references in the literature[1] to a colloidal, polymeric form of plutonium (IV), formed in aqueous solution at acidities below ~0·2 M. Earlier work has been recently reviewed by OCKENDEN and WELCH,[2] who have discussed the formation and properties of the colloid and have made estimates of its molecular weight in dilute nitric acid. During work[3] on the ion exchange reactions of quadrivalent plutonium in diethylene glycol dibutyl ether,† it became clear that a similar polymer can form in this solvent following the hydrolysis of plutonium (IV) nitrate species extracted from aqueous solution. The properties and mode of formation of this polymer are discussed below, and comparisons made with analogous behaviour in aqueous solution.

EXPERIMENTAL

Materials

An aqueous solution of plutonium nitrate was prepared by warming a solution of plutonium in 8 M nitric acid with hydrogen peroxide, in order to reduce any plutonium (VI) present. The solution was warmed on a water-bath until decomposition of excess peroxide was complete.

Analytical grade nitric and perchloric acids were used, diluted as required: concentrations were determined by titration against standard sodium hydroxide solution.

Butex was purified by the method already described.[4]

Organic solutions

Solutions of nitric and perchloric acids in Butex were prepared by shaking the pure solvent with the appropriate aqueous solution, followed by centrifuging to separate the phases completely. The upper (organic) layer was then removed with a pipette.

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† For convenience, this solvent will be referred to by the trade name "Butex". In a previous publication,[4] the name "dibutylcarbitol" was used.

(1) J. C. HINDMAN *The Actinide Elements, National Nuclear Energy Series* Vol. IV–14A, p. 317. McGraw-Hill, New York (1956).
(2) D. W. OCKENDEN and G. A. WELCH *J. chem. Soc.* 3358 (1956).
(3) D. G. TUCK and G. A. WELCH To be published.
(4) D. G. TUCK *J. chem. Soc.* 3202 (1957).

Portions of the stock plutonium nitrate solution in 8 M nitric acid were stirred with roughly equal volumes of Butex already 3 M in nitric acid. The separated organic phase was then diluted with solvent or nitric acid in butex to give solutions of suitable acidity and/or optical density. The plutonium concentration in such solutions was determined by α-counting after suitable dilution, using the technique of periphery heating.[5]

Spectrophotometry

The absorption spectra of certain solutions were measured on a Hilger "Uvispek" spectrophotometer, using 1 cm glass cells. Pure solvent was used as a "blank".

X-ray examination

Samples of precipitated polymer, prepared by heating solutions of low nitric acid concentration, were examined by X-ray powder photography. The details of the technique have been given elsewhere.[6]

RESULTS AND DISCUSSION

Colour changes in plutonium solutions in Butex

As a preliminary to spectrophotometric examination the colours and colour changes of a solution of plutonium in Butex, (concentration approximately 0·5 mg/ml) were studied at various nitric acid concentrations in the solvent. Equilibrium aqueous acidities are given in parentheses.

0·015 M (0·48 M) HNO_3	: brown solution; after 1½ days, a green precipitate was visible.
0·095 M (0·87 M)	: brown solution, noticeably green after 1½ days.
0·42 M (1·58 M)	: brown solution, rather paler than at 0·095 M; some traces of green after 1½ days.
1·30 M (2·84 M)	: pale green solution,
1·71–3·2 M (3·40–5·9 M)	: green solutions, quite stable.

The green colour of the strong acid solutions was quite different from the rather dirty yellow-green which developed in weak acid media. Similar examinations were carried out on perchloric acid solutions in Butex.

0·03 M (0·46 M) $HClO_4$	: brown solution, rapidly going green (~10 min), and finally producing a green precipitate after 2 hr.
0·91 M (1·74 M)	: brown solution, quite stable over at least 2 hr; some slight colour change detected later.
2·45 M (4·57 M)	: brown solution, apparently quite stable over period of examination (10 hr).

In these latter experiments, plutonium was added as plutonium nitrate solution; it was not possible to carry out experiments in the complete absence of nitrate (see Part II). The stability of plutonium species in weak nitric acid (0·15 M) has also been examined over a longer period (plutonium concentration 4 mg/ml).

Initially	light brown.
1 day	much deeper brown.
5 days	green colour just apparent.
13 days	definitely green-brown.
37 days	green colour predominant.
100 days	totally yellow-green.

[5] D. G. Tuck *Analyt. chem. acta* **17**, 271 (1957).
[6] B. J. MacDonald and J. B. Fardon *J. chem. Soc.* 781 (1956).

Spectrophotometric examination

The absorption spectra of two solutions of plutonium in weak nitric acid solutions in Butex, of different ages, are shown in the Fig. 1.

The absorption maxima are summarized below, and assignments made on the basis of the data given by HINDMAN[7] for aqueous $PuNO_3^{3+}$ (404, 420, 447, 476,

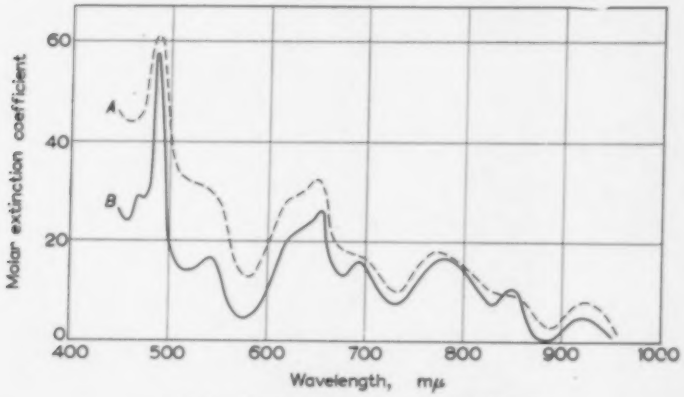

Fig. 1.—Absorption spectra of Pu(IV) in Butex.
A—0·15 M HNO_3, 83 days after dilution.
B—0·3 M HNO_3, 1 day after dilution.

544, 660, 703, 795 and 855 mμ) and by OCKENDEN and WELCH[2] for aqueous colloidal plutonium (IV) (510, 580, 615, 690, 740, 825, 910 and 1045 mμ).

This spectral evidence, together with that from the colour changes described above, suggests that the species initially formed on reducing the acidity of a plutonium (IV)

Wavelength (mμ)	Occurrence	Assignment
470	*B*	$Pu(NO_3)_4$
488	*A*, *B*	$Pu(NO_3)_4$
545	*B*	$Pu(NO_3)_4$
620	*A*, *B* (shoulders)	colloid
653	*A*, *B*	$Pu(NO_3)_4$
697	*A* (weak), *B*	colloid
774	*A*	? (shift from 782 mμ ?)
782	*B*	$Pu(NO_3)_4$
853	*A* (very weak), *B*	$Pu(NO_3)_4$
920	*A*, *B*	colloid

nitrate solution in Butex by dilution, is $Pu(NO_3)_4$ (or some close derivative). This is in agreement with the prominent absorption at 488 mμ in the spectra, since HINDMAN[8] has pointed out that the 476 mμ peak due to $PuNO_3^{3+}$ in aqueous solution shifts to higher wavelengths with increasing complexing by nitrate ion, moving eventually to 491 mμ for the ion $Pu(NO_3)_6^-$. Plutonium tetranitrate is apparently

[7] J. C. HINDMAN *The Actinide Elements, National Nuclear Energy Series* Vol. IV-14A, p. 339. McGraw-Hill, New York (1956).
[8] J. C. HINDMAN *The Actinide Elements, National Nuclear Energy Series* Vol. IV-14A, p. 340. McGraw-Hill, New York (1956).

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unstable in weak nitric acid, and perchloric acid, solutions in Butex forming first a hydroxy complex and eventually a polymer. The mechanism of these processes is discussed below.

Stability of polymeric plutonium in butex

On heating a solution of polymeric plutonium (IV) in Butex, a green-brown precipitate is formed; the stability to precipitation at ~100°C appears to depend on the age of the solution and on the acidity. X-ray examination of the washed and dried material showed it to be almost completely amorphous; a few lines were found exactly analogous to those in the X-ray pattern of the amorphous plutonium "hydroxide" precipitated by adding excess ammonia to fresh aqueous plutonium nitrate solution[2]. In one experiment, a few μl of a brown aqueous phase, shown to contain $Pu(NO_3)_4$ or some derivative, was also thrown out of the organic solution.

In a further experiment, polymer precipitated as described above was left in contact with the mother liquor, which still contained appreciable amounts of plutonium in solution, for three weeks. The X-ray pattern of the dried precipitate was quite different from that of the previous sample, and showed that the crystal size was much larger. Although the lines were still quite diffuse, they could be indexed on face centred cubic systems with lattice parameters of approximately 5·6, 4·4 and 4·1 Å; of these, the first is the most well-defined and could be due to a partially hydrated plutonium dioxide structure ($a = 5{\cdot}4$ Å for anhydrous PuO_2). The perfecting of the crystal structure of precipitates under similar conditions in aqueous systems has been demonstrated by KOLTHOFF[9] who suggests that the process involves the elimination of solvent sheaths between neighbouring particles of the precipitate. It appears that this can also occur in organic solutions, probably along with some crystal growth by "Ostwald ripening". If the present behaviour is indeed parallel to that in aqueous systems, the freshly precipitated material is a polymeric plutonium "hydroxide" of disordered crystal structure, containing occluded solvent which is eliminated on prolonged digestion in the cold.

Heating this dried precipitated polymer in a quartz vessel with a Meker burner results in an immediate decrepitation with violent loss of some component, leaving a more compact black powder. X-ray analysis showed that this was finely divided crystalline plutonium dioxide.

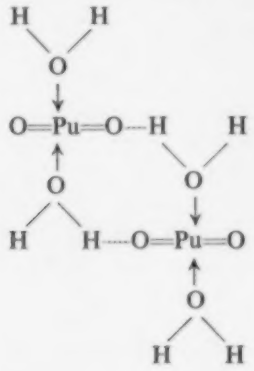
A sample of a solution of plutonium nitrate in weak nitric acid (0·15 M) was centrifuged after standing at room temperature for three months. After 2½ hr at 7000 g, only negligible amounts of solid were apparent. This behaviour may be due either to a much lower molecular weight than that found in aqueous solutions[2] or to a much higher solubility of the polymer in Butex.

Hydrolysis of plutonium tetranitrate

It is clear that the formation of polymeric plutonium hydroxide in Butex solution is due to hydrolysis of $Pu(NO_3)_4$. It has been shown elsewhere[4,10] that a solution of nitric acid in this solvent, prepared by extraction of aqueous solutions, contains water both as $HNO_3{\cdot}H_2O$ and as "free" H_2O. Hydrolysis of $Pu(NO_3)_4$ in such a system can bring about successive replacement of NO_3^- by OH^- leading to a $Pu(OH)_4$

[9] I. M. KOLTHOFF *et al.*; for a review of this work, see A. C. WAHL and N. A. BONNER *Radioactivity Applied to Chemistry*, p. 38 *et seq.* John Wiley, New York (1951).
[10] E. GLUCKAUF and H. A. C. MCKAY, quoted by MCKAY *J. inorg. nucl. Chem.* **4**, 375, (1957).

species. It is suggested that this plutonium hydroxide rearranges to $PuO_2 \cdot 2H_2O$ which can dimerize by hydrogen-bonding. The structure postulated is



The present work gives no evidence as to the molecular weight of the polymer in Butex solution, but this structure can clearly lead to addition of further units. Since water is only weakly bound into this structure, strong heating would cause loss of H_2O with formation of plutonium dioxide, as is actually observed.

Acknowledgements—Helpful discussions are acknowledged with B. J. MACDONALD, who carried out the X-ray analysis, and with D. W. OCKENDEN and G. A. WELCH.

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BOOK REVIEWS

G. H. MORRISON and H. FREISER: **Solvent Extraction in Analytical Chemistry**. Wiley, New York, Chapman and Hall, London. 269 pp., 54*s*.

SOLVENT extractions have been used for separations in analytical chemistry on an increasing scale in recent years and the only collected data on this technique available to the analytical chemist has occurred in review articles. The need for a comprehensive text book on solvent extraction has existed for several years and the appearance of this book helps to fill a gap in the literature which has occurred for too long. The authors have divided the contents of their book into four parts. In the first part the principles of solvent extraction are given a fairly comprehensive treatment, and apparatus and general techniques are considered in the second part. There is much useful practical information for the analytical chemist and the reviewer can support the employment of radioisotopes to facilitate the study of new solvent extraction methods. The apparatus described is sufficient to meet the needs of most chemists wishing to use this technique.

Various extraction systems are described in the third part. In the ion association systems good coverage of the literature is given, although some omissions were noticed. Reference to the work on the newer trialkylphosphine oxides is very welcome. With the chelate systems a fuller treatment would have been more appropriate. Reagents such as cupferron and sodium diethyldithiocarbamate are very widely used for separations in analytical chemistry and worthy of a more detailed treatment. In the fourth part details are given of selected procedures which have been used for the extraction of various elements. Much information is given, but little attempt has been made to help the analyst in choosing the most suitable system when several alternatives are available. Also some of the information is not as up-to-date as one should expect in a new book. For example, there is no reference to data on the solvent extraction of plutonium from nitrate solutions which is reported in *Nucleonics* **13**, 60 (1955). In conclusion, analytical chemists will find this book useful, but a more critical treatment of some parts of it would have enhanced its value.

G. W. C. MILNER

J. J. KATZ and G. T. SEABORG: **The Chemistry of the Actinide Elements.** Methuen, London, 1957. XV + 508 pp., 63*s*.

THE first major release of information concerning the transuranium elements was in the two volumes entitled *The Transuranium Elements* issued in the National Nuclear Energy Series (Div. IV–14B) in 1949. This was followed by a survey volume, *The Actinide Elements*, in the same Series (Div. IV–14A) in 1954. Since the publication of the latter book, four new heavy elements have been synthesized (einsteinium to nobelium) and considerable extensions have been made to our knowledge of the properties of the previously known actinides. The present book brings the whole subject up to date and achieves a greater clarity by virtue of being written as a composite whole rather than as a collection of papers on diverse topics by many individuals.

The Transuranium Elements was primarily a record of the vast amount of data collected by American scientists in the preceding nine years. KATZ and SEABORG have now given us a more balanced presentation of the chemistry of the whole series of elements from actinium to nobelium. The increasing spread of experimental activity in this field is reflected in the fact that nearly 30 per cent of the references cited in the chapter on plutonium are from non-American sources.

After a short introductory chapter, the chemistry of each of the elements from actinium to curium is described separately. There follows a general chapter on the trans-curium elements, and the final chapter correlates the chemical and physical properties of the whole series in terms of the "actinide

concept". There are three Appendices, listing the atomic weights of the longer-lived actinide nuclei up to einsteinium, X-ray energies of the elements from thorium to curium, and nuclear spins of nuclei from ^{227}Ac to ^{243}Am.

The chapters on the individual elements contain a short historical introduction; a section, where applicable, on the occurrence in nature, and a list of the decay characteristics of the known isotopes; sections on separation and purification, on the chemistry and crystal structure of the solid compounds, and on the ions in solutions. The aqueous chemistry of those of the actinide elements which can exist in several oxidation states is very complex and the relationships between the oxidation states present problems not encountered to a similar degree in any of the lighter elements. An extensive account is given of these relationships and of the complexing and hydrolytic properties of the ions.

The authors are to be congratulated on their condensation of the available information into a single volume of less than 500 pages of text. The result is a very readable account of the subject. Since the text is supported by most of the literature references which have appeared in the past ten years, and by subject and name indices, the book will prove to be a very welcome reference volume for the specialist in this field. The style, however, is such that it will also be of great value to any chemist who wishes to become acquainted with these new, important elements.

J. K. Dawson

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CURIUM–249

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(*Received* 27 *May* 1957)

Abstract—The assignment of the 65 min β-activity in curium to ^{249}Cm has been confirmed by neutron irradiations of curium containing 86 per cent ^{246}Cm. The half-life and maximum β-particle energy of ^{249}Cm were found to be 64 $\pm$ 3 min and 0·86 $\pm$ 0·10 MeV, respectively. The yield of ^{249}Cm from the irradiations corresponds to a capture cross-section of about 6 barns for ^{246}Cm.

THE study of MTR-irradiated Pu and thermonuclear test debris has shown that ^{249}Cm is a fairly short-lived β-emitter.[1,2,3] When curium from the debris of the thermonuclear explosion was irradiated in MTR a curium isotope, thought to be ^{249}Cm, was produced. Its half-life and maximum β-particle energy were 65 min and 0·9 MeV.[3]

For our studies of the properties of ^{246}Cm and ^{248}Cm we isolated curium which contains 86 per cent ^{248}Cm and 14 per cent ^{246}Cm, plus traces of ^{245}Cm and ^{247}Cm.[4] Since this was much richer in ^{248}Cm than the curium from the thermonuclear test debris we irradiated our sample in the MTR in order to confirm and extend previous work on ^{249}Cm. From these experiments we obtained a value of 64 $\pm$ 3 min for the half-life and 0·86 $\pm$ 0·10 MeV for the maximum β-particle energy of ^{249}Cm. The yield corresponds to a pile-neutron capture cross-section for ^{248}Cm of about 6 barns.

The curium sample was produced by α-decay of californium obtained from MTR-irradiated plutonium.[4] The curium was separated from the californium by ion-exchange using Dowex-50 eluted with 0·4 M ammonium α-hydroxy *iso*butyrate at pH 4·1.[5] A small amount of ^{242}Cm tracer was added to the curium in order to determine the yields. The amount of ^{248}Cm was determined by α-counting and α-pulse analysis; the half-life previously reported[4] was used for the calculation.

The curium was then irradiated for about 1 hr in a flux of 2×10^{14} n/cm^2 sec in MTR. After the irradiation the curium was purified as quickly as possible by co-precipitations with CeF_3 and by ion-exchange methods. The drops from the ion-exchange column were collected individually and after evaporation to dryness were α- and β-counted. A 64 $\pm$ 3 min β-activity was found which followed curium in the separation procedures and which had the same elution characteristics as the α-active curium. The main β-activity in all the drops containing curium α-activity decayed

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† The Knolls Atomic Power Laboratory is operated by the General Electric Company for the U.S. Atomic Energy Commission under Contract No. W-31-109 Eng. 52.

[1] S. G. THOMPSON, A. GHIORSO, B. G. HARVEY and G. R. CHOPPIN, *Phys. Rev.* **93**, 908 (1954).
[2] H. DIAMOND, L. B. MAGNUSSON, J. F. MECH, C. M. STEVENS, A. M. FRIEDMAN, M. H. STUDIER, P. R. FIELDS and J. R. HUIZENGA, *Phys. Rev.* **94**, 1083 (1954).
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[4] J. P. BUTLER, T. A. EASTWOOD, H. G. JACKSON and R. P. SCHUMAN, *Phys. Rev.* **103**, 965 (1956).
[5] G. R. CHOPPIN, B. G. HARVEY and S. G. THOMPSON, *J. inorg. nucl. Chem.* **2**, 22 (1956).

with a 64 min half-life. The absorption curve of the β-particles in aluminium is shown in Fig. 1. Two components are present and both decay with the 64 min half-life. The maximum β-particle energy of the more energetic component, as determined by comparison with ^{198}Au and ^{36}Cl, is $0{\cdot}86 \pm 0{\cdot}10$ MeV. The yield of ^{249}Cm corresponds to a capture cross-section of about 6 barns for ^{248}Cm, in reasonable agreement with the previously reported value of 4 barns.[6]

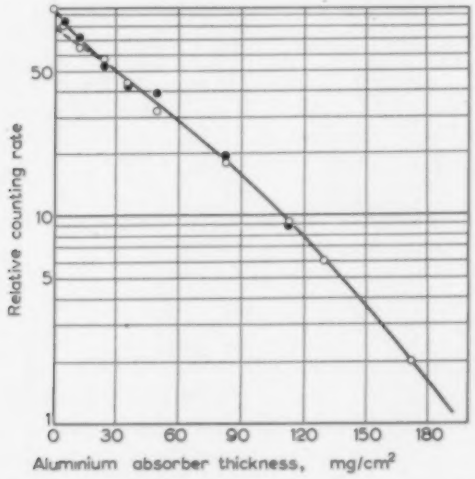

FIG. 1.—^{249}Cm absorption curve. The open and closed circles represent results obtained from two different drops in the curium fraction from the ion-exchange column purification.

A second irradiation using the same curium also yielded a 64 min activity and gave the same capture cross-section for ^{248}Cm.

Our irradiation confirms the mass assignment of the 64 min activity to ^{249}Cm since our curium, unlike the thermonuclear test curium, contains mainly ^{248}Cm and no ^{250}Cm.

Acknowledgements—The assistance of Dr. J. P. BUTLER, who helped separate some of the curium from its parent californium, and the MTR staff, particularly C. HOGG, A. S. RICHARDSON and S. D. REEDER who a.ranged the irradiations, supplied the counters and much of the chemical equipment, is gratefully acknowledged.

[6] G. T. SEABORG Private communication to J. R. HUIZENGA, *International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Paper P/809; Vol. 7, p. 261. United Nations (1956).

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NUCLEAR-CHARGE DISTRIBUTION IN FISSION: CUMULATIVE YIELDS OF SHORT-LIVED KRYPTON AND XENON ISOTOPES FROM THERMAL-NEUTRON FISSION OF ^{235}U*

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(*Received* 25 *October* 1957)

Abstract—Experiments are described in which use was made of the very large emanating powers of barium stearate and uranyl stearate for determination of cumulative yields for a number of krypton and xenon isotopes formed in the thermal-neutron fission of ^{235}U. The results, expressed as the fraction of the total chain yield, are: ^{89}Kr, 0·960 ± 0·004; ^{90}Kr, 0·86 ± 0·02; ^{91}Kr, 0·59 ± 0·01; ^{92}Kr, 0·31 ± 0·01; ^{139}Xe, 0·82 ± 0·02; ^{140}Xe, 0·59 ± 0·01; ^{141}Xe, 0·21 ± 0·02; ^{143}Xe, (8·5 ± 0·5) × 10^{-3}; ^{144}Xe, (1·1 ± 0·1) × 10^{-3}.

These data along with previously reported independent-yield data are used for construction of an empirical curve of the most probable primary charge (Z_p) vs. mass number. In the regions where shell edges are absent the curve is about equidistant for complementary mass numbers from the most stable charge (Z_A) lines for light and heavy fragments as proposed in the postulate of equal-charge displacement; in the regions where shell edges are present the Z_p curve makes a smooth continuous transition. The Z_p curve tends to approach and remain close to the 50-proton shell edge.

It is proposed and some evidence is presented that the charge distribution curve (for a given mass number) is distorted for uranium fission in the regions near $Z = 50$ and $Z = 42$ because the 50–42 proton split is favoured, at least partly at the expense of the 51–41 and 49–53 proton splits.

QUANTITATIVE information about nuclear-charge distribution in low-energy fission[1,2] has been limited to the independent yields of about a dozen nuclides that are near stability and are shielded by stable or relatively long-lived isobars. Information about the independent or cumulative yields of early members of the fission chains has not been obtained because of the very short half-lives involved.

Attempts were made[3] to determine the cumulative yields of some of the short-lived krypton and xenon isotopes by gas-sweeping a solution of uranium undergoing fission, and although periods as short as one second were detected in the gas, quantitative removal of the inert gases from solution was not achieved. Workers in HAHN's laboratory had found,[4] similarly, that although 3·83 day radon (^{222}Rn) could be removed quantitatively from solution by boiling or sweeping, the 51·5 sec thoron (Tn, ^{220}Rn) could not. For determination of Tn they incorporated its parent ThX (^{224}Ra) into solid barium palmitate, $Ba(C_{16}H_{31}O_2)_2$, which emanates 98 to 99 per cent

* This work done under the auspices of the U.S. Atomic Energy Commission.

(1) E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, pp. 3–14. United Nations (1956).
(2) A. C. PAPPAS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, pp. 19–26 United Nations (1956); AECU-2806 (1953).
(3) C. R. DILLARD, R. M. ADAMS, H. FINSTON and A. TURKEVICH, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN). NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 624. McGraw-Hill, New York (1951).
(4) O. HAHN, *Applied Radiochemistry* p. 197, Cornell University Press (1956).

of the Tn. STRASSMAN[5] had found previously that the emanating powers of barium salts of fatty acids increased with chain length. Later, GREGORY and MOORBATH[6] showed that the emanating power of barium stearate, $Ba(C_{18}H_{35}O_2)_2$, for Tn was 100 per cent.

The above information indicated that the short-lived krypton and xenon fission products would escape efficiently (perhaps quantitatively) from barium or uranyl stearate. Two experiments were tried, one in which uranyl stearate was irradiated,

TABLE 1.—FRACTION OF FISSION CHAIN ESCAPING FROM VARIOUS MEDIA

Inert gas	Descendant determined	Swept U soln.		Uranyl stearate[a]	Barium stearate[b]
		ref. 3	ref. 8		
3·2-m ^{89}Kr	50·4-d ^{89}Sr	0·92	0·52	0·94	0·95
33-s ^{90}Kr	27·7-y ^{90}Sr	—	0·30	0·84	0·85
9·8-s ^{91}Kr	9·7-h ^{91}Sr	0·38	0·15	0·58	0·58
3·0-s ^{92}Kr	2·7-h ^{92}Sr	—	0·03	0·32	0·30
16-s ^{140}Xe	12·8-d ^{140}Ba	0·39	0·23	0·59	0·58

[a] Compared to $UO_2(NO_3)_2.6H_2O$.
[b] Compared to Al recoil catcher.

and one in which recoil fragments from a thin ^{235}U deposit were caught in barium stearate. The fraction of a fission chain escaping was determined by comparing the amount of a late member of a chain (e.g. 50·4 day ^{89}Sr) found in the stearate salt with the amount found in a non-emanating material* (uranyl nitrate hexahydrate or an aluminium catcher for recoil fragments) irradiated at the same time in the same neutron flux. ^{99}Mo, which will be shown to have negligible formation from an inert-gas ancestor, was the internal standard. The chemistry was similar to that used in later runs and described in the appendix. The results, summarized in Table 1 along with some gas-sweeping results for comparison, show that uranyl stearate and barium stearate are indeed highly emanating materials. They emanate the inert-gas fission products with about equal efficiency and more efficiently than the gas-swept aqueous solutions.

If the emanating power of the stearate salts were 100 per cent for the various krypton and xenon isotopes listed, the values in Table 1 would be the cumulative yields of the inert gases expressed as fraction of total chain yield. The results described in the accompanying paper[9] on the emanating power of barium stearate for 3·9 sec actinon (An, ^{219}Rn) suggest that this is nearly but not quite correct. It is shown that An does escape quantitatively from the tiny grains of barium stearate powder and that the emanating power for An is >99 per cent for very thin layers and for thicker layers

* Inorganic salts and metals have very low (<1 per cent) emanating powers.[4,7]

[5] F. STRASSMAN, *Z. phys. Chem.* B **26**, 362 (1934).
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[7] A. C. WAHL, *Radioactivity Applied to Chemistry* (Edited by A. C. WAHL and N. A. BONNER) Chap. 9, p. 284. John Wiley, New York, (1951).
[8] R. M. ADAMS and H. FINSTON, *Radiochemical Studies: Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1791. McGraw-Hill, New York (1951).
[9] A. C. WAHL and E. R. DANIELS, *J. inorg. nucl. Chem.* **6**, 278 (1958).

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in vacuum. However, in air from $\simeq$10 mg/cm^2 of barium stearate, as was used to stop the recoil fragments, only 90 to 95 per cent escapes. Therefore, experiments were designed for irradiation in vacuum, and these are described below.

EXPERIMENTAL

Two thin ^{235}U deposits were irradiated back to back in the evacuated container diagramed in Fig. 1. The fission products recoiling from one deposit were stopped in an aluminium foil from which the inert gases did not escape, and those from the other were stopped in barium stearate powder from which the inert gases did escape into the large evacuated space above. There the inert gases decayed, depositing their descendants on the filter-paper liner. Comparison of the descendent activities found on the liner, in the barium stearate, and in the aluminium gave the fractional cumulative yields of the inert gases. Experimental details are given in the following paragraphs.

Irradiation container

The irradiation container, diagramed in Fig. 1, was machined from pure (2-S) aluminium rod. Care was exercised in selecting the rod for purity, since some impurities (e.g., Cu and Mn) would have

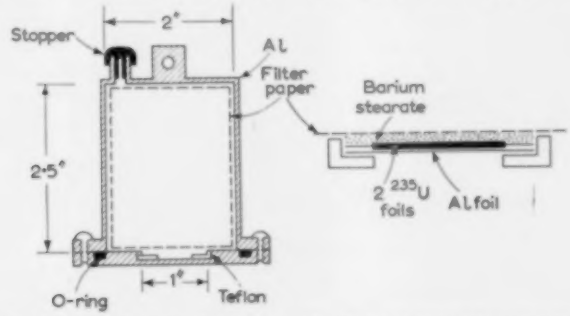

FIG. 1.—Left: Cross-sectional view of cylindrical irradiation container.
Right: Enlarged cross-sectional view of sample arrangement in the teflon holder.

caused the container to be too "hot" to handle conveniently after an irradiation. The container was evacuated, and air was readmitted after irradiation, through a hypodermic needle inserted through the serum bottle stopper (sleeve type). With the needle withdrawn, the container held a vacuum ($<$0·3 mm Hg) for several days as KENNEDY[10] had observed. The irradiation container was lined with Whatman No. 41H filter paper. In run II a filter-paper shield (8 mg/cm^2) was inserted between the liner and the barium stearate.

The irradiation container was designed so that the total volume was $>$200 times the volume of the barium stearate powder. Tests, described in the appendix, showed that only 0·5 $\pm$ 0·2 per cent of the 3·9 sec An that escaped from the barium stearate grains decayed in the pores of the powder (calculated for uniform distribution throughout all free space, 0·4 per cent). The tests also showed that 98 $\pm$ 3 per cent of the active deposit was collected on the filter-paper liner.

The ^{235}U plates were electrodeposited[11] on platinum in 2·0 cm diameter disks and flamed. Each contained about 0·4 mg of ^{235}U (from enriched uranium, $>$ 90 per cent ^{235}U). The 0·2 mg/cm^2 thickness of the U_3O_8 deposits was small compared to the recoil ranges of the fission fragments, so a large fraction of the fragments escaped (calculated: 0·493 for mass 89 and 0·491 for mass 144). The thicknesses of the aluminium foil (9·6 mg/cm^2) and barium stearate powder ($\simeq$ 14 mg/cm^2) were large compared to the ranges (Table 2).

Barium stearate

The barium stearate was prepared by slow addition of warm sodium stearate solution to excess barium chloride solution. The details are given in the accompanying paper.[9] Two preparations were

[10] J. W. KENNEDY, Private communication.
[11] B. WARREN, Uranium-235, LA-1721, compiled by J. KLEINBERG, Unpublished (1956).

used, B′ in run I and B in run II. These were prepared in identical ways except AcX was incorporated in B to allow the determination of its emanating power, which was found[9] to be >99 per cent for An. The AcX had decayed before preparation B was used in run II.

TABLE 2.—FISSION FRAGMENT RANGES

Material	Ranges, mg/cm²	
	Mass 89	Mass 144
Al[a]	3·7	2·5
U_3O_8[b]	7·6	5·4
$Ba(C_{18}H_{35}O_2)_2$[b]	2·7	1·8

[a] See FINKLE *et al.*[12]
[b] Calculated by method of FRIEDLANDER and KENNEDY[13] on the assumption that relative atomic stopping powers for fission fragments are the same as those for alpha particles.

Irradiation

The assembled irradiation container was evacuated through a No. 24 hypodermic needle inserted through the rubber stopper. During evacuation the container was maintained at a temperature of ≃60° C by an electrical heating tape wrapped around it. This served to out-gas the filter paper and barium stearate so that during the irradiation at a temperature of ≃50° C further out-gassing would be minimized. Pumping and heating over night reduced the pressure to <0·3 mm of Hg.

The evacuated container was irradiated for 2 hr in a thermal-neutron flux of $\simeq 5 \times 10^{11}$ cm^{-2} sec^{-1} in the Los Alamos Homogeneous Reactor. After a 30–40 min cooling period for 2·3 min ^{28}Al and the short-lived fission products to decay, the pressure in the container was checked (and found to be 2 mm of Hg in both runs), air was admitted, and the container opened.

Chemistry

The aluminium recoil catcher (fraction A), the barium stearate (fraction B), and the filter-paper liner (fraction C) were dissolved separately, and the resulting solutions were diluted to 50·0 ml with water and nitric acid to give 2 N HNO_3 solutions of the fission products. Aliquots of these solutions were taken for determination of the fission-product activities. Single samples were run on fractions B and C; duplicates were run on fraction A, and these checked very well. The dissolving and separation procedures are described in the appendix.

The four samples were run in parallel so that the chemical separations occurred at the same times. Since growth and decay corrections were the same, the activities of the samples could be compared at any time. No appreciable error due to the different genetic histories of the samples was introduced by this procedure because the periods of the inert gases and their predecessors are very small compared to the periods of the nuclides measured.

Calculations

For a given nuclide, the sum of the activities found in fractions B (barium stearate) and C (filter-paper liner) was a little smaller than the activity found in fraction A (aluminium). This was caused in part by the non-quantitative transfer of the barium stearate from the irradiation container to the dissolving vessel (several per cent was estimated to be lost), in part by the non-quantitative collection of the active deposit on the filter-paper liner (for example, decay of an inert gas in the small volume beneath the stopper (Fig. 1) would give little active deposit on the paper), and in part, perhaps, by fewer recoil fragments coming from the ^{235}U deposit facing the barium stearate than from the deposit facing the aluminium. Since none of these factors could be evaluated accurately, internal standards were used for normalization of the activities found in the three fractions to the same number of fission fragments.

[12] B. FINKLE, E. J. HOAGLAND, S. KATCOFF and N. SUGARMAN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 471. McGraw-Hill, New York (1951).
[13] G. FRIEDLANDER and J. W. KENNEDY, *Nuclear and Radiochemistry* p. 190. John Wiley, New York (1955).

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^{99}Mo was used as internal standard for fraction B, and ^{89}Sr was used for fraction C. Essentially none (<0·05 per cent) of the ^{99}Mo was found in fraction C, so the ratio of ^{99}Mo in fraction A to ^{99}Mo in fraction B served as the normalization factor for fraction B. The ratio of ^{89}Sr in fraction A to ^{89}Sr in fraction C was multiplied by the fraction of the 89 chain that escaped from the barium stearate (one minus the normalized ratio of ^{89}Sr in fraction B to ^{89}Sr in fraction A) to give the normalization factor for fraction C. The normalization factors are listed in Table 3.

TABLE 3.—NORMALIZATION FACTORS*

Fraction	Run I	Run II
B (barium stearate)	1·045	1·150
C (filter-paper liner)	1·036	1·118

* (For normalization to the same number of fission fragments as collected in fraction A.)

The larger normalization factors for run II were found to be due mainly to the presence of some fission activity in the shield, the piece of filter paper between the barium stearate and the filter-paper liner. Based on the activities in the aluminium catcher, 6·3 per cent each of ^{89}Sr, ^{140}Ba, ^{141}Ce, and ^{144}Ce were found in the shield. Because the inert-gas ancestors of these fission products differ so greatly in half-life and in cumulative yield, the equivalence of these activities leads to the conclusions that their presence was due to direct recoil into the shield and that the emanating power of the filter paper was essentially zero. The irradiation container must have been jarred prior to the irradiation to open a hole in the barium-stearate catcher and thus to expose a portion of the shield to recoiling fission fragments. No recoil fragments reached the liner (in either run) as shown by the absence of ^{99}Mo activity in the liner. Thus, the recoil fragments in the shield did not contribute to the activities of either the barium stearate or liner, and, therefore, did not affect the results.

For the normalization factors determined for single chains to be appropriate for other chains, the same fraction of the chains must have escaped by recoil from a ^{235}U deposit. As has been discussed, the thickness of the deposits was chosen so that this was essentially true in spite of differences in recoil ranges. Further evidence on this point was obtained from calculations of the recoil yields in the aluminium catcher for several chains relative to the mass-99 chain. In these calculations appropriate growth and decay corrections were made, fission yields recommended by STEINBERG and GLENDENIN[1] were used, and beta counting efficiencies were estimated from an empirical efficiency vs. energy curve constructed by PRESTWOOD and BAYHURST[14] by comparison of the external proportional counter with a 4-π counter. The results of the calculations are listed in Table 4. Within the uncertainties of the calculations the recoil yields were equal. This equality confirms that there was little or no emanation from the aluminium catcher of the inert gas ancestors of the nuclides determined.

TABLE 4.—RECOIL YIELDS IN ALUMINIUM CATCHER RELATIVE TO ^{99}Mo RECOIL YIELD

Nuclide determined	Relative recoil yield
^{89}Sr	0·99
^{139}Ba	1·01
$^{140}Ba + {}^{140}La$	0·94

RESULTS

The fractions of the various fission-product chains formed from inert gases that escaped from the barium stearate are listed in Table 5. A value was calculated by dividing the normalized activity of the inert-gas descendant found in fraction C

[14] R. J. PRESTWOOD and B. BAYHURST, Private communication.

TABLE 5.—FRACTION OF FISSION CHAIN FORMED FROM INERT GAS THAT ESCAPED FROM BARIUM STEARATE

Inert gas	Descendant determined	Fraction from inert gas		Recovery (%)	
		Run I	Run II	Run I	Run II
^{89}Kr (3·2 min)	^{89}Sr (50·4 days)	0·954	0·958	—	—
^{90}Kr (33 sec)	^{90}Sr (27·7 years) → ^{90}Y (64·0 hr)	0·846	0·863	101	104
^{91}Kr (9·8 sec)	^{91}Sr (9·7 hr) → ^{91}Y (57·5 days)	0·583	0·593	96	97
^{92}Kr (3·0 sec)	^{92}Sr (2·7 hr) → ^{92}Y (3·5 hr)	0·310	0·315	98	98
?	^{99}Mo (67 hr)	<0·0005	<0·0005	—	—
^{139}Xe (41 sec)	^{139}Ba (85 min)	0·813	0·822	—	—
^{140}Xe (16 sec)	^{140}Ba (12·8 days) + ^{140}La (40 hr)	0·588	0·595	101	101
^{141}Xe (1·7 sec)	^{141}Ce (31 days)	0·195	0·213	92	101
^{143}Xe (1.0 sec)	^{143}Ce (33 hr)	0·0083	0·0088	100	100
^{144}Xe (≃1 sec)	^{144}Ce (282 days) + ^{144}Pr (17·5 min)	0·00112	0·00103	96	97

(filter-paper liner) by the sum of the normalized activities found in fractions C and B (barium stearate).

The occurrence of the ^{138}Ba (n, γ) ^{139}Ba reaction in the barium stearate prevented measurement of the ^{139}Ba from fission in fraction B, so the fraction of the 139 chain that escaped was obtained by division of the normalized ^{139}Ba activity found in the liner by the ^{139}Ba activity found in the aluminium.

As a measure of the precision of the results the last column of Table 5 lists the recoveries relative to the aluminium recoil catcher; the sum of the normalized activities found in the barium stearate and liner was divided by the activity found in the aluminium catcher.

Multiplication of the fractional values listed in Table 5 by 1·004 corrects for the fraction of empty container space in the barium stearate powder and gives the fractional cumulative yields of the inert gases. The averages of the values obtained and their estimated uncertainties are listed in Table 6. The uncertainties were estimated from the internal consistency of the results, the estimated reliability of the radiochemical determinations, and the uncertainty in the emanating power of barium stearate for the fission-product inert gases. It has been shown[9] that the barium-stearate preparation used in run II had an emanating power for 3·9 sec An of >99 per cent and the preparation used in run I was prepared by the same method.[9] Krypton and xenon, being lighter and smaller than radon, diffuse faster, and therefore, for isotopes with half-lives ≧3·9 sec there must have been >99 per cent escape. For

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the inert gases with 1 sec half-lives the escape must have been >96 per cent, a value readily calculated from the mean-life of $\leqq 0{\cdot}06$ sec[9] for an inert gas in the preparation. Since 3·2 min ^{89}Kr is relatively long lived, the assumption was made that it escaped quantitatively.

DISCUSSION

The postulate of equal charge displacement

For comparison with the experimentally determined fractional cumulative yields there are listed in Table 6 the values predicted from the empirical postulate of equal-charge displacement.[15] This postulate has been more successful[1,2,15] than other

TABLE 6.—FRACTIONAL CUMULATIVE YIELDS

Fission product	Cumulative yield, fraction of total chain yield			
	Experimental	Equal-charge-displacement postulate		
		GLENDENIN *et al.*[15]	PAPPAS[2]	STEINBERG and GLENDENIN[1]
^{89}Kr	0·960 ± 0·004	0·93	0·91	0·94*
^{90}Kr	0·86 ± 0·02	0·82*	0·81*	0·87*
^{91}Kr	0·59 ± 0·01	0·60*	0·64*	0·64*
^{92}Kr	0·31 ± 0·01	0·40	0·45	0·45
^{139}Xe	0·82 ± 0·02	0·78*	0·60	0·69
^{140}Xe	0·59 ± 0·01	0·55*	0·43	0·51
^{141}Xe	0·21 ± 0·02	0·31	0·25*	0·17*
^{143}Xe	$(8{\cdot}5 \pm 0{\cdot}5) \times 10^{-3}$	$3{\cdot}5 \times 10^{-3}$	$5{\cdot}3 \times 10^{-3}$	$2{\cdot}3 \times 10^{-3}$
^{144}Xe	$(1{\cdot}1 \pm 0{\cdot}1) \times 10^{-3}$	$1{\cdot}2 \times 10^{-3}$*	7×10^{-5}	3×10^{-4}

* Agrees with the experimental value within the sum of the experimental and theoretical uncertainties, the latter corresponding to ±0·1 in Z_P.

proposals in accounting for independent yield data, the only data that have been available concerning nuclear charge division. It is assumed in the postulate that:

(1) The most probable mode of charge division leads to equal ideal chain lengths for the light and heavy fragments,

$$(Z_A - Z_P)_{\text{light}} = (Z_A - Z_P)_{\text{heavy}},$$

Z_P being the most probable charge and Z_A being the most stable charge for the particular mass number.

(2) All fission product chains (in low energy fission) have the same symmetrical charge-distribution curve (see Table 8 in the appendix).

In the various interpretations of the postulate essentially the same charge-distribution curve is used; the differences are in the methods of obtaining Z_P. In the original postulate GLENDENIN *et al.*[15] used a continuous Z_A function and, therefore, obtained a continuous Z_P function. PAPPAS[2] used a Z_A function that was discontinuous at shell edges and, therefore, obtained a Z_P function that was discontinuous. STEINBERG and GLENDENIN[1] used this same discontinuous Z_A function but took

[15] L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 489. McGraw-Hill, New York (1951).

average values in the regions of shell edges and obtained a Z_P function with twice as many but smaller discontinuities. A minor difference in the interpretations is that PAPPAS[2] considered the primary fragments before neutron boil-off; the others considered the fragments after neutron boil-off. As can be seen in Table 6 the agreement between the experimental and predicted values is reasonably good, but no one modification of the postulate gives completely satisfactory agreement.

The krypton and xenon isotopes studied are in the regions just above the 50- and 82-neutron shell edges, regions in which excessive neutron boil-off may occur[1,2] from nuclides with 1, 3, 5, or 7 neutrons in excess of 50 or 82. Such excessive neutron boil-off would result in low independent yields for odd N nuclides and high independent yields for even N nuclides (assuming the primary fragments are formed with the normal distribution of charge). Comparison of the values in Table 6 gives no support to this proposal. Approximately one half of the discrepancies that do exist between the experimental and theoretical values are in the wrong direction.

The empirical Z_P function

Because of the uncertainty about the proper method of calculating the Z_P function, it was of interest to determine it empirically. It was assumed, as in the postulate of equal-charge displacement, that the same charge-distribution curve (Table 8 in the appendix) is appropriate for all fission chains. Then from each cumulative-yield value reported in this paper and from each independent-yield value that has been determined[1,2,16-20] an empirical Z_P value was obtained (see Table 9 in the appendix). These are plotted in Fig. 2, in which the light and heavy regions are folded so that the total $Z = 92$ and the total $A = 233{\cdot}5$ ($\nu = 2{\cdot}5$). A smooth continuous curve passes through all the points except those for mass numbers 96 and 98, and reasonable explanations for these discrepancies will be given. Some general features of the empirical Z_P curve are of interest:

(1) In the regions where the Z_A functions are not influenced by shell edges, the Z_P curve is approximately equi-distant (for complementary mass numbers) from the two Z_A lines as proposed in the postulate of equal charge displacement. The Z_A lines shown are those proposed by CORYELL.[21]

(2) In the regions where the Z_A functions are discontinuous due to crossing of the 50 and 82 neutron shell edges, the Z_P curve makes a smooth continuous transition. There are no large discontinuities in the Z_P function as proposed by PAPPAS.[2]

(3) The Z_P line tends to approach and remain close to the 50-proton shell edge as proposed by KENNETT and THODE.[16] However, there is no pronounced tendency for it to remain close to the 82 (or 50) neutron shell as they proposed.

^{96}Nb and ^{98}Tc

The two points in Fig. 2 which deviate from the smooth curve were obtained from the small independent yields of the shielded nuclei ^{96}Nb and ^{98}Tc. The deviations

[16] T. J. KENNETT and H. G. THODE, *Phys. Rev.* **103**, 323 (1956).
[17] G. W. REED, *Phys. Rev.* **98**, 1327 (1955).
[18] A. C. WAHL, *Phys. Rev.* **99**, 730 (1955).
[19] S. KATCOFF and W. RUBINSON, *Phys. Rev.* **91**, 1458 (1953).
[20] G. D. O'KELLY and Q. V. LARSON, Abstracts Southwide Amer. Chem. Soc. Meeting, Memphis, (1956).
[21] C. D. CORYELL, *Annual Review of Nuclear Science* Vol. 2, p. 305. Annual Reviews, Inc., Stanford, Calif. (1953).

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could be due to uncertainties in the Z_P function, errors in the independent yield values, or perturbations in the charge-distribution curve.

PAPPAS[2] accounted for the small independent yield of ^{96}Nb by extending the portion of his linear but discontinuous Z_P function starting at $A = 88$ to $A = 96$ and having the discontinuity occur between $A = 96$ and $A = 97$. This Z_P line would pass through the point at $A = 96$, but it would miss the points at $A = 139$ and $A = 140$ in Fig. 2, and could not reasonably be extended to $A = 98$.

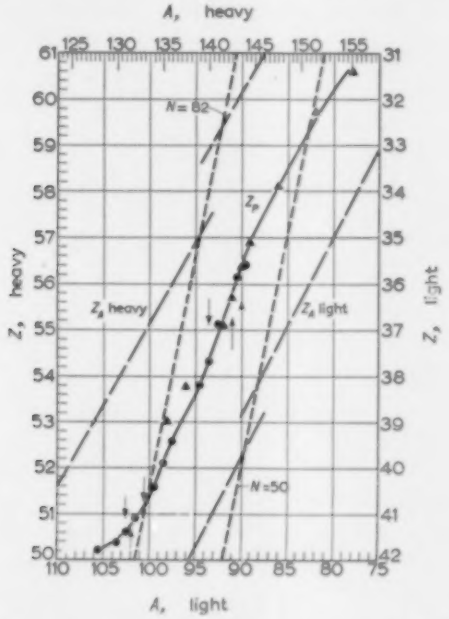

FIG. 2.—The empirical Z_P function. ● heavy fission products; ▲ light fission products; upper limits indicated by tips of arrows. The Z_A lines are those proposed by CORYELL.[21]

Isomerism is expected for both ^{96}Nb and ^{98}Tc due to the proximity of low- and high-spin states. The observed low independent yields for the known nuclides could be caused by essentially all of the direct formation giving the unknown isomers (which would be assumed not to decay to the known state).

For ^{98}Tc the charge-distribution curve was extrapolated considerably to reach the very small value of the independent yield, and part of the discrepancy could be due to uncertainties in the extrapolation.

For both ^{96}Nb and ^{98}Tc there is a possibility of deviation from the smooth charge-distribution curve because of perturbations caused by the 50-proton shell. This possibility is discussed below.

The charge-distribution curve

The charge-distribution curve[1,2] (given in the appendix) is an empirical curve which was drawn[15] to fit a few independent-yield data (all for different chains or fission processes) for which Z_P values were calculated according to the postulate of

equal-charge displacement.[15] As more independent yield data became available (for still different chains or fission processes, and only one yield per chain) the combination of the curve and postulate (with minor modifications[1,2]) was still remarkably successful. However, there was no direct evidence that the curve itself was correct for any specific chain. The first evidence of this kind is for the 141 chain. The Z_P value calculated from the 0·21 fractional cumulative yield of ^{141}Xe is 55·1, and that from the $\simeq$0·02 fractional independent yield[22] of ^{141}La is $\simeq$55·0, in satisfactory agreement.

It seems reasonable, however, that the charge-distribution curve may be distorted for fission chains in the regions near $_{50}$Sn and its complement $_{42}$Mo (for $_{92}$U fission) because of a favoured 50–42 proton split, analogous to the favoured 82–62 neutron split, which is evidenced by fine structure[1] in the mass-yield curve near $A = 100$ and $A = 134$. If a favoured 50–42 proton split were at least in part at the expense of the adjacent 51–41 and 49–43 proton splits then for $_{92}$U fission there would result high independent yields for $_{42}$Mo and $_{50}$Sn isotopes and low independent yields for $_{41}$Nb, $_{43}$Tc, $_{49}$In and $_{51}$Sb, consistent with the observed low independent yields of ^{96}Nb and ^{98}Tc. In support of this proposal, preliminary results[23] indicate that the ^{97}Nb independent yield from thermal-neutron fission of ^{235}U is also low, and for ^{97}Nb it is known that the 1 min isomer decays to the 72 min isomer, on which measurements are made.

Conclusion

The empirical Z_P function (Fig. 2) used with the charge-distribution curve (Table 8) gives a good correlation of most charge-distribution data for thermal-neutron fission of ^{235}U. Use of the empirical function for prediction of unmeasured independent or cumulative yields eliminates one of the two assumptions made in the postulate of equal-charge displacement and also the accompanying uncertainties in calculation of Z_P values near shell edges. In order to account for the low independent yields of $^{96}_{41}$Nb, $^{97}_{41}$Nb, and $^{98}_{43}$Tc the proposal is made that the 50-proton shell affects charge division in fission, the 50–42 proton split being favoured in uranium fission at least partly at the expense of the adjacent 51–41 and 49–43 proton splits.

For other fission processes insufficient data are available for application of the empirical treatment described in this paper. However, the few data there are and results of the treatment for ^{235}U do suggest that a smooth continuous Z_P function, such as that proposed by GLENDENIN *et al.*[15] should be used rather than a discontinuous one, such as proposed by PAPPAS.[2] Allowance probably should be made for the 50-proton shell both in distortion of the Z_P function and in distortion of the charge-distribution curve.

Added Note

GRUMMITT and MILTON[24] have recently reported values of $<8 \times 10^{-5}$ and 7×10^{-4} for the fractional independent yields of ^{90}Y and ^{140}La, respectively, formed from thermal-neutron fission of ^{235}U. The upper limit for ^{90}Y is entirely consistent with the normal charge-distribution curve and the empirical Z_P function discussed in this paper. The ^{140}La value is somewhat higher (corresponding to a charge displacement of 0·2) than the value predicted from the normal charge-distribution curve fitted to

[22] G. P. FORD and C. W. STANLEY, AECD-3551 Unpublished (1953).
[23] D. E. TROUTNER and A. C. WAHL, Unpublished results from Washington University.
[24] W. E. GRUMMITT and G. M. MILTON, *J. inorg. nucl. Chem.* **5**, 93 (1957).

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the Z_P value calculated from the ^{140}Xe cumulative yield. This small discrepancy may indicate that the charge-distribution curve for the 140 chain is slightly broader than the normal curve.

GRUMMITT and MILTON[25] also proposed a fourth variation of the equal-charge displacement postulate. It gives a smooth continuous Z_P curve, which agrees reasonably well with the empirical Z_P curve. This new modification gives, as do the others, correct predictions ($\pm 0{\cdot}1$ charge unit) for about half of the measured krypton and xenon cumulative-yield values, and there is no correlation between the discrepancies and the odd- and even-neutron nuclei.

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APPENDIX

Test of irradiation container

The emanating power of a barium stearate preparation containing AcX was determined in the evacuated irradiation container and in a large evacuated desiccator. Approximately 100 mg of barium stearate, spread in a teflon dish to a uniform thickness ($\simeq$20 mg/cm^2) and covered with filter paper (Whatman No. 41H) to prevent back deposit,[19] was allowed to stand in an evacuated vessel at least 6 hr for establishment of secular equilibrium between 36·1 min AcB and 11·7 day AcX. The vacuum was then broken, and the activity of AcB in the barium stearate was measured and compared with the AcB activity of the sample under non-emanating conditions. The lead-sulphide method which is described in detail in the accompanying paper,[19] was used. The results are summarized in the following table.

The absolute values of the emanating power may be in error by as much as 0·5 per cent, the uncertainty being due mostly in the time of separation of AcB from AcX, but since the same procedure was used in all runs the relative values are believed reliable to $\pm 0{\cdot}2$ per cent.[19]

From the data in Table 7 the following conclusions may be drawn.

(1) The emanating power of the barium stearate preparation was $\geq$99·5 per cent.

(2) In the irradiation container the emanating power drops $0{\cdot}5 \pm 0{\cdot}2$ per cent which is accounted for by the fact that the pores of the powder make up 0·4 per cent of the free volume of the container.

TABLE 7.—EMANATING POWER OF BARIUM STEARATE FOR An

Vessel	Pressure (mm Hg)	Emanating power (per cent)	
Irradiation container	<0·3	99·7	99·7
Irradiation container	2·5	99·7	
Large desiccator	<0·3	100·2	100·2
Large desiccator	<0·3	100·1	
Large desiccator	<0·3	99·2*	

* A single 110 mg lump of barium stearate as filtered and dried (dimensions $\simeq$1 cm long and $\simeq$0·5 cm in diameter).

[25] W. E. GRUMMITT and G. M. MILTON, CRC-694, AECL No. 453 (1957).

(3) The escape of An from barium stearate powder is as efficient at 2·5 mm pressure as it is at $<0{\cdot}3$ mm.

(4) The degree to which a barium stearate preparation is powdered does not greatly affect its emanating power. The size of the precipitated crystals must be very small and the filtered and dried mass must be very porous for 99 per cent of the An to escape from the single solid lump.

In another experiment at 2·5 mm pressure the fractions of AcB collected on the filter-paper liner and on the shield were determined. It was found that 98 ± 3 per cent deposited on the liner and <1 per cent on the shield. The 3 per cent error is the estimated uncertainty of the radiochemical determination.

Chemistry and counting

Dissolution of fractions. The aluminium recoil catcher (fraction A) was dissolved in 1 ml of 6 N HCl, 5 ml of 90 per cent HNO_3 was added to destroy chloride ion, and the solution diluted to 50·0 ml.

The barium stearate (fraction B) was gently charred, burned, and then ignited to remove the organic matter. The residue was dissolved in a little dilute nitric acid, and after addition of 6 ml of 16 N HNO_3 the solution was diluted to 50·0 ml.

The filter-paper liner (fraction C) was dissolved in 20 ml of boiling 90 per cent HNO_3. After addition of 6 ml of 60 per cent $HClO_4$ the solution was boiled down to fumes of $HClO_4$, 1 ml portions of 90 per cent HNO_3 being added immediately if the fuming $HClO_4$ turned black, and the evaporation again carried to HClO-fumes. The concentrated $HClO_4$ solution was cooled, 3 ml of 16 N HNO_3 was added, and the solution diluted to 50·0 ml.

(1) ^{139}Ba, ^{140}Ba ($+^{140}$La). Barium was separated[26] from 0·200 ml of stock solution by three barium-chloride precipitations, a ferric-hydroxide and a lanthanum-hydroxide scavenging precipitation, and one barium-chromate precipitation. It was weighed as barium chromate, and the decay was followed on a methane-flow beta-proportional counter. The 85 min ^{139}Ba was obtained from the initial portion of the curve after subtraction of the ^{140}Ba and ^{140}La contributions. The 12·8 day ^{140}Ba activity was obtained from later portions of the curve after the 40 hr ^{140}La was in transient equilibrium.

(2) ^{91}Sr→^{91}Y, ^{92}Sr→^{92}Y. Strontium was separated[27] from 4·00 ml of stock solution by two strontium-nitrate precipitations, one ferric-hydroxide and two barium-chromate scavenging precipitations, and two strontium-carbonate precipitations, which were separated by an yttrium-hydroxide scavenging step. Strontium carbonate was weighed, and, after the yttrium daughters had grown in over night, yttrium was separated from strontium by three yttrium-hydroxide precipitations (the first two in the presence of strontium carrier) and one yttrium-oxalate precipitation.[28] The oxalate was ignited to yttrium oxide, which was weighed and counted. The beta decay curve was resolved into the 3·5 hr ^{92}Y and 57·5 day ^{91}Y components. A very low intensity tail ($\simeq$15 counts/m) due to the presence of $\simeq$1 per cent thorium in the yttrium carrier, was subtracted.

(3) ^{143}Ce. Before the strontium-nitrate precipitations in procedure (2), cerium carrier had been added and the solution heated 30 min to promote exchange.[29] Cerium in the strontium-nitrate supernatants was purified[30] by extraction of cerium (IV) into methyl *iso*butyl ketone from aqueous nitric acid solution, back extraction, and precipitation of cerium(III) oxalate two times, the last precipitate being ignited[31] and weighed as cerium dioxide. The gamma activity was followed on a sodium-iodide scintillation counter through 3·8 g/cm^2 of lead, which very effectively reduced the ^{141}Ce and ^{144}Ce activities.

(4) ^{89}Sr. After the 9·7 hr ^{91}Sr and 2·7 hr ^{92}Sr had decayed the strontium from procedure (2) was further purified by two yttrium-hydroxide scavenging precipitations and a strontium carbonate precipitation. The strontium carbonate was weighed and counted. The beta decay curve was resolved into the 50·4 day ^{89}Sr and a low-intensity long-lived component (mostly ^{90}Sr + ^{90}Y).

(5) ^{90}Sr→ ^{90}Y. After complete decay of ^{91}Sr and ^{92}Sr, strontium was separated from 30·0 ml of stock solution (two 15·0 ml portions of A) by the procedure outlined in (2), modified to include an

[26] C. O. MINKKINEN, LA-1721, p. 169, compiled by J. KLEINBERG, Unpublished (1954).
[27] L. E. GLENDENIN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1460. McGraw-Hill, New York (1951).
[28] C. W. STANLEY, LA-1721, p. 105, Compiled by J. KLEINBERG, Unpublished (1954).
[29] J. W. GRYDER and R. W. DODSON, *J. Amer. chem. Soc.* **73**, 2890 (1951).
[30] L. E. GLENDENIN, K. F. FLYNN, R. F. BUCHANAN and E. P. STEINBERG, *Analyt. Chem.* **27**, 59 (1955).
[31] D. P. AMES, LA-1721, p. 174, compiled by J. KLEINBERG, Unpublished (1954).

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TABLE 8.—FRACTIONAL CHAIN YIELDS FOR THERMAL FISSION

$Z - Z_P$	Independent	Cumulative	$Z - Z_P$	Independent	Cumulative
−3·8	$1·1 \times 10^{-7}$		−1·1	0·207	0·217
−3·7	2·2		−1·0	0·244	0·264
−3·6	4·0		−0·9	0·276	0·314
−3·5	8·0		−0·8	0·307	0·358
−3·4	$1·6 \times 10^{-6}$		−0·7	0·337	0·404
−3·3	3·0		−0·6	0·369	0·452
−3·2	6·0		−0·5	0·398	0·501
−3·1	$1·3 \times 10^{-5}$		−0·4	0·424	0·548
−3·0	2·2		−0·3	0·442	0·596
−2·9	4·0		−0·2	0·461	0·642
−2·8	8·0		−0·1	0·469	0·686
−2·7	$1·6 \times 10^{-4}$		0·0	0·472	0·736
−2·6	3·0		0·1	0·469	0·783
−2·5	6·0		0·2	0·461	0·819
−2·4	$1·2 \times 10^{-3}$		0·3	0·442	0·846
−2·3	2·6		0·4	0·424	0·876
−2·2	5·0		0·5	0·398	0·897
−2·1	$1·0 \times 10^{-2}$		0·6	0·369	0·917
−2·0	2·0		0·7	0·337	0·933
−1·9	3·5		0·8	0·307	0·949
−1·8	5·1		0·9	0·273	0·965
−1·7	6·7		1·0	0·244	0·980
−1·6	8·3		1·1	0·210	0·990
−1·5	0·102	0·103	1·2	0·176	0·995
−1·4	0·123	0·124	1·3	0·151	0·997
−1·3	0·151	0·154	1·4	0·123	0·999
−1·2	0·176	0·181	1·5	0·102	0·999

additional barium chromate and an additional yttrium hydroxide scavenging step. After growth of 64 hr ^{90}Y, it was separated from strontium by four yttrium hydroxide precipitations. Because of the low intensity (20–100 counts/min), additional purification was necessary from the ≃1 per cent thorium impurity discovered in the yttrium carrier after it had been added. A zirconium iodate precipitation[21] removed thorium, ThX (^{224}Ra) remained with strontium in the yttrium hydroxide supernatants, and ThB (^{212}Pb) and ThC (^{212}Bi) were carried by lead sulphide. Yttrium was precipitated as the oxalate,[28] which was ignited, and the oxide was weighed and counted. The beta decay curves all showed 64 hr half-lives.

(6) ^{141}Ce, ^{144}Ce ($+^{144}Pr$). After decay of the 33 hr ^{143}Ce, cerium from the strontium-nitrate supernatant in procedure (5) was purified as outlined in procedure (4). (The cerium carrier had been added and the solution heated to promote exchange[29] before the strontium-nitrate precipitation.) The beta decay curves were resolved* after a year to give the 31 day ^{141}Ce and 282 day ^{144}Ce components. This resolution did not give accurate values for the very low intensity ^{144}Ce ($+^{144}Pr$) activity in fraction C, so all the samples were followed an additional year through 75 mg/cm² of aluminium, which eliminated the remaining ^{141}Ce activity. Once a month the samples were counted in succession four times, the C samples and background receiving 2 hr counts each time. Counting rates were determined from the total counts recorded. The decay of all samples including the C samples, which were only ≃4 counts/min above a 15 counts/min background, was appropriate for the 282 day half-life.

(7) ^{99}Mo. Molybdenum was separated[22] from 1·00 ml of stock solution (4·00 ml of fraction C)

* The decay curve was resolved by a method suggested by G. P. FORD and described by WAHL.[18]

[22] C. O. MINKKINEN, LA-1721, p. 122, Compiled by J. KLEINBERG, Unpublished (1954).

Nuclear-charge distribution data

TABLE 9.—INDEPENDENT AND CUMULATIVE YIELDS (THERMAL-NEUTRON FISSION OF ^{235}U)

Fission product	Fractional chain yield[a]		$Z - Z_P$	Z_P	Ref.
	Independent	Cumulative			
$^{78}_{33}As$	0·09		1·57	31·43	*b*
$^{82}_{35}Br$	$\simeq 6 \times 10^{-4}$		~2·5		*c*
	$1·4 \times 10^{-4}$		2·72	32·3	*d*
	$1·6 \times 10^{-4}$		2·70		*e*
$^{86}_{37}Rb$	$1·2 \times 10^{-5}$		3·10		*e*
	$1·5 \times 10^{-6}$		3·06	33·92	*f*
$^{89}_{36}Kr$		0·960	0·86	35·14	*g*
$^{90}_{36}Kr$		0·86	0·35	35·65	*g*
$^{90}_{39}Y$	$<3 \times 10^{-4}$		>2·6		*h*
	$<5 \times 10^{-4}$		>2·5	<36·4	*e*
$^{91}_{36}Kr$		0·59	−0·32	36·32	*g*
$^{91}_{39}Y$	$<9 \times 10^{-3}$		>2·1	<36·9	*h*
$^{92}_{36}Kr$		0·31	−0·90	36·90	*g*
$^{98}_{41}Nb$	9×10^{-5}		2·80		*e*
	$1·4 \times 10^{-4}$		2·72	38·24	*i*
$^{98}_{43}Tc$	3×10^{-6}		4·0	39·0	*j*
$^{102}_{45}Rh$	$<2 \times 10^{-7}$		>3·7	<41·3	*k*
$^{128}_{53}I$	$1·0 \times 10^{-4}$		2·78	50·22	*c*
$^{130}_{53}I$	$2·8 \times 10^{-4}$		2·62	50·38	*c*
$^{131}_{52}Te$	0·14		1·35		*l*
	0·15 ± 0·07		1·1 to 1·6	50·6	*m*
	0·04 − 0·12		1·4 to 1·9		*n*
$^{131}_{53}I$	<0·01		>2·1	<50·9	*n*
$^{132}_{52}Te$	0·36 ± 0·17		0·0 to 1·2	50·8 to 52·0 } 50·9	*o*
$^{132}_{53}I$	<0·01		>2·1	<50·9 }	*n*
$^{133}_{53}I$	<0·05		>1·8	<51·2	*n*
$^{133}_{54}Xe$	<0·001		>2·4	<51·6 } <51·2	*p*
$^{134}_{53}I$	0·13		1·40		*f*
	0·11		1·48	51·56	*n*
$^{135}_{54}Xe$	0·035		1·90		*p*
	0·049		1·80	52·1	*q*
	0·027		1·96		*r*
$^{136}_{55}Cs$	$1·0 \times 10^{-3}$		2·42		*f*
	9×10^{-3}		2·44	52·57	*e*
$^{139}_{54}Xe$		0·82	0·20	53·80	*g*
$^{140}_{54}Xe$		0·59	−0·32	54·32	*g*
$^{140}_{57}La$	<0·03		>1·9	<55·1	*s*
$^{141}_{54}Xe$		0·21	−1·12	55·12 } 55·1	*g*
$^{141}_{57}La$	≃0·02		≃2·0	≃55·0 }	*t*
$^{143}_{54}Xe$		$8·5 \times 10^{-3}$	−2·13	56·13	*g*
$^{144}_{54}Xe$		$1·1 \times 10^{-3}$	−2·40	56·40	*g*
$^{148}_{61}Pm$	$<10^{-4}$		<2·8	<58·2	*e*

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by five molybdenum α-benzoinoxime precipitations, three ferric-hydroxide scavenging precipitations, and one precipitation of lead molybdate, which was weighed and counted. A very small activity (≃15 counts/min), decaying with an ≃67 hr half-life, was found in the C samples. If this activity was due to ^{99}Mo formed from decay of escaped ^{99}Kr, the fraction of the 99 chain formed from escaped ^{99}Kr would have been $3{\cdot}3 \times 10^{-4}$ and $3{\cdot}4 \times 10^{-4}$ from runs I and II, respectively. These values are ≃2000 times the value predicted from the empirical Z_P curve (Fig. 2) and the charge-distribution curve (Table 8), and since ^{99}Mo in the filter paper could have come from molybdenum impurity by the n, γ reaction or from contamination of the filter paper by "hot" barium stearate, the values are used only to set an upper limit of 5×10^{-4} for the fraction of the 99 chain coming from escaped ^{99}Kr.

The normal charge-distribution curve

Essentially the same symmetrical charge-distribution curve originally proposed by GLENDENIN *et al.*[15] has been used by all investigators. For convenience in relating $(Z - Z_P)$ to both independent and cumulative yields, Table 8 has been prepared. The independent-yield values listed by PAPPAS[2] were normalized so that those for $(Z - Z_P)$ values differing by one unit add to $1{\cdot}000 \pm 0{\cdot}001$.

FOOTNOTES TO TABLE 9

a Based on measured total chain yield.[1]
b N. SUGARMAN, *Phys. Rev.* **89**, 570 (1953).
c KENNETT and THODE.[16]
d M. H. FELDMAN, L. E. GLENDENIN and R. R. EDWARDS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 598. McGraw-Hill, New York (1951).
e COOK.[1,2]
f L. E. GLENDENIN, *Tech. Report No.* 35, M.I.T. (1949).
g This paper.
h REED.[17]
i J. S. GILMORE, Private communication.
j O'KELLY and LARSON.[20]
k J. A. SWARTOUT and W. H. SULLIVAN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 856. McGraw-Hill, New York (1951).
l L. E. GLENDENIN, Private communication.
m PAPPAS.[2]
n WAHL,[18] Data for ^{131}Te corrected for the 5% ^{131}Sb decaying to ^{131}Te (reference *l*).
o A. C. PAPPAS, *Tech. Report* **63**, M.I.T. (1953).
p KATCOFF and RUBINSON.[19]
q E. J. HOAGLAND and N. SUGARMAN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1030 McGraw-Hill, New York (1951).
r F. BROWN and L. YAFFE, *Canad. J. Chem.* **31**, 242 (1953).
s N. SUGARMAN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Record, Div. IV, Vol. 9, p. 1139. McGraw-Hill, New York (1951).
t FORD and STANLEY.[22]

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 278 to 287. Pergamon Press Ltd., London

EMANATING POWER OF BARIUM STEARATE FOR 3·9-SECOND ACTINON (^{219}Rn)*

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Abstract—The emanating power of barium stearate powder for actinon is >99 per cent for thin layers in air at atmospheric pressure and for ≃10 mg/cm² layers at reduced pressures (≤7·5 mm Hg). The emanating power decreases with increasing pressure and with increasing thickness at atmospheric pressure. The method of preparation of the highly emanating barium stearate and two methods of measurement of the emanating power are described. Some preliminary results on gas sweeping of actinon and thoron from aqueous solution are also given.

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THIS investigation was initiated to find efficient methods for the removal of short-lived inert gases from liquids or solids. Such methods would be of use for determination of cumulative yields of short-lived krypton and xenon fission products (see the preceding paper[1]). In work[2,3] on the Manhattan Project, uranyl nitrate solutions undergoing neutron irradiation were swept with nitrogen, but the results indicated that the short-lived Kr and Xe isotopes were not removed quantitatively. We started a study of the efficiency of gas sweeping aqueous solutions using 51·5 sec thoron (Tn, ^{220}Rn) and 3·9 sec actinon (An, ^{219}Rn), and the preliminary results obtained are reported in this paper. However, this study was abandoned in favour of emanating-power studies of barium stearate because of promising preliminary results on the escape of the short-lived fission-product inert gases from barium stearate and uranyl stearate (see Table 1 in the preceding paper[1]).

GREGORY and MOORBATH[4] had found that the emanating power of barium stearate for 51·5 sec thoron was 100 per cent (no estimate of error given) for temperatures above 20°C and concluded the escape must be mainly by diffusion from the solid grains. We have studied the emanation of 3·9 sec actinon from barium stearate. Barium stearate was chosen rather than uranyl stearate because it seemed almost certain that the barium salt would carry AcX (^{223}Ra), the parent of actinon, by isomorphous replacement.[5,6] For uranyl stearate the method by which AcX would be carried seemed uncertain, and if carrying were by surface adsorption the emanation results would be misleading.

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[1] A. C. WAHL, *J. inorg. nucl. Chem.* **6**, 263 (1958).
[2] C. R. DILLARD, R. M. ADAMS, H. FINSTON and A. TURKEVICH, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 624. McGraw-Hill, New York (1951).
[3] R. M. ADAMS and H. FINSTON, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1791. McGraw-Hill, New York (1951).
[4] J. N. GREGORY and S. MOORBATH, *Trans. Faraday Soc.* **47**, 1064 (1951).
[5] O. HAHN, *Applied Radiochemistry* p. 69. Cornell University Press (1936).
[6] N. A. BONNER and M. KAHN, *Radioactivity Applied to Chemistry* (Edited by A. C. WAHL and N. A. BONNER) Chap. 6, p. 105. John Wiley, New York (1951).

EXPERIMENTAL

Preparation of barium stearate

GREGORY and MOORBATH[4] precipitated barium stearate (a) by neutralization of an alcoholic solution of stearic acid with aqueous barium hydroxide and (b) by mixing warm aqueous solutions of potassium stearate and barium chloride. We preferred method (b) but used sodium stearate, which was more readily available to us. The solutions were kept warm (60–75°C), to prevent formation of sodium-stearate gel, and approximately neutral (the pure salt solutions were satisfactory), to prevent stearic acid precipitation in acid or formation of barium carbonate from carbon dioxide of the air in basic solution. The sodium-stearate solution was added slowly to excess* of the barium chloride solution undergoing mechanical stirring. Too rapid stirring resulted in a colloidal suspension, and even at moderate stirring rates some colloid formed. The coagulated precipitate was washed with water by decantation until colloidal material was removed; then the precipitate was filtered on Whatman No. 41H paper, washed with water, and air dried at room temperature. The filtration was rapid if colloidal material was absent. The dried preparation was chopped to a powder with the edge of a spatula.

Other than keeping the solutions warm and approximately neutral, the barium ion in excess, and mixing slowly with stirring, we did not find the conditions critical. Preparations B and B′, which were used in the cumulative-yield measurements[1], were each a mixture of five batches prepared by addition of 50 ml of 0·5 per cent sodium stearate (0·016 M) to 50 ml of 0·011 M barium chloride (≃33 per cent excess) over a period of 1·5 min. The initial temperature of the solutions was ≃75°C, and some cooling occurred during mixing. The chemical yield was ≃45 per cent based on sodium stearate. The preparation used in the tests of the irradiation container[1] was made by addition of 150 ml of 1 per cent sodium stearate (0·033 M) to 145 ml of 0·020 M barium chloride solution (15 per cent excess) over a period of 20 min. The temperature of the reaction mixture was maintained at 60°C. Colloidal material was not removed by decantation, and filtration was slow. The chemical yield was ≃80 per cent based on sodium stearate. Both procedures gave preparations with >99 per cent emanating power for actinon. Other preparations prepared under slightly different conditions also had emanating powers for actinon of >99 per cent.

AcX (^{223}Ra) was separated from Ac (^{227}Ac) and RdAc (^{227}Th) by being carried with barium through several barium chloride precipitation steps[8] and at least one lanthanum hydroxide or ferric hydroxide scavenging step. AcX was co-precipitated with barium stearate but tended to concentrate in the solution; in one preparation the ratio of AcX to Ba in barium stearate was ≃0·7 of the ratio in the original barium chloride solution.

Measurement of emanating power

For convenience of reference the main branch of the actinium series starting with AcX is shown in Fig. 1. The minor branches (0·3 per cent and less) are not important for the accuracy achieved and are omitted for simplicity.

The emanating-power of a preparation was determined by comparison of the beta activity of the active deposit (descendants of actinon) in the preparation under emanating and non-emanating conditions.[9,10] The relationship is

$$E = 1 - A_E/A_N \qquad (1)$$

in which E is the emanating-power, A_E is the equilibrium activity of the active deposit in the sample under emanating conditions, and A_N is the equilibrium activity of the active deposit in the sample under non-emanating conditions.

The radiation measured was the β-rays from AcB and AcC″. Methane-flow beta-proportional

* STRASSMAN[7] reported that in the preparation of barium palmitate excess palmitate ion resulted in an unfilterable precipitate.

[7] F. STRASSMAN, *Z. phys. Chem.* **B 26**, 362 (1934).
[8] L. E. GLENDENIN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1657. McGraw-Hill, New York (1951).
[9] O. HAHN, *Applied Radiochemistry* p. 193. Cornell University Press (1936).
[10] A. C. WAHL, *Radioactivity Applied to Chemistry* (Edited by A. C. WAHL and N. A. BONNER) Chap. 9, p. 296. John Wiley, New York (1951).

counters were used for all measurements. Two methods of determining A_E and A_N were used and are described below.

PbS Method. In this method AcB was separated as PbS from the sample, and the decay of AcB with AcC″ in transient equilibrium was followed. The barium-stearate sample, which had been under emanating conditions for at least 6 hr for establishment of secular equilibrium, was dissolved by being shaken with a mixture of $CHCl_3$ (10 ml) and 3·5 M HNO_3 (5 ml) containing carrier Pb^{++} (40 mg). The $CHCl_3$ phase containing the stearic acid was removed, a solution (5 ml) saturated with H_2S

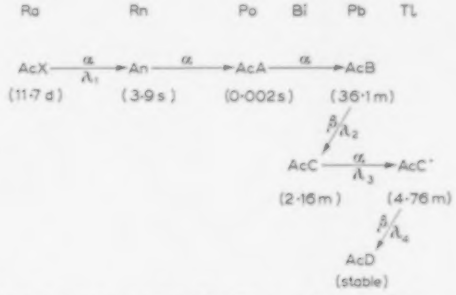

FIG. 1.—Principal descendants of AcX (^{223}Ra). Minor (<0·3 per cent) branches are not shown.

was added, and the PbS was filtered (No. 42H paper). (The conditions given were used for the series of experiments in which the irradiation container was tested;[11] in other experiments smaller volumes and less carrier were used with good results.) The decay curve of the PbS precipitate was followed, and the straight portion (36·1 min half-life) was extrapolated back to the time of separtaion of AcB from AcX (taken as the mean time of filtration). The activity A at separation time is related to A_E and A_N by the expression

$$A = A_E e^{-\lambda_2 t} + A_N(1 - e^{-\lambda_2 t}) \tag{2}$$

in which λ_2 is the decay constant of AcB and t is the time interval between solution of the barium-stearate sample and the separation of AcB from AcX. During this time interval the emanating-power of the sample was assumed to be zero.

The filtrate was boiled to expel H_2S and evaporated to dryness. Lead carrier and nitric acid were added and diluted to the volume of the original aqueous solution (5 ml), and the vessel containing the solution was stoppered and allowed to stand at least 6 hr under these non-emanating conditions. A solution saturated with H_2S was added, and PbS was filtered and counted as before. The activity A' at separation is related to A_N, the activity under non-emanating condition at the time the barium stearate sample was dissolved, by the relationship

$$A' = A_N e^{-\lambda_1 t'} \tag{3}$$

in which λ_1 is the decay constant of AcX and t' is the time interval between solution of the barium-stearate sample and the second AcB–AcX separation.

Combination of equations (1), (2) and (3) gives

$$E = e^{\lambda_2 t}\left[1 - \frac{A}{A'} e^{-\lambda_1 t'}\right]. \tag{4}$$

Typical data, taken during the test of the irradiation container at 2·5 mm of Hg pressure (Appendix of preceding paper[11]), are given below:

$t = 1{\cdot}37$ min (duration of first filtration = 0·73 min)
$t' = 0{\cdot}964$ day (duration of second filtration = 0·70 min)
$A = 835$ counts/min
$A' = 27{,}200$ counts/min
$E = 1{\cdot}027\ [1 - (0{\cdot}0307)\ (0{\cdot}942)] = 0{\cdot}997.$

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The principal source of error for the large emanating-power values measured was the uncertainty in t, the time during which growth of AcB occurred under the non-emanating conditions of the solution. An error in E of 0·004 would have been caused by a 0·2 min error in t; it is doubtful that the uncertainty in t was greater than this. A 5 per cent error in the relative activities or chemical yields of the two PbS samples would have caused an error in E of only 0·0015. From these considerations it was concluded that the absolute values of emanating power were accurate to $\pm$0·005. For comparison of two samples, since the same procedure was used and any errors in timing would tend to cancel, the difference between two emanating-power values was probably reliable to $\pm$0·002.

Covered method. Another method for determination of emanating-power involved simply the covering of an emanating sample with a material (aluminium) that was impervious to actinon and following the growth of the active-deposit beta activity.[9,10] A_E in equation (1) was obtained by extrapolation of the growth curve back to the time of covering, and A_N was obtained from equation (3) in which A' represents the measured activity at a time t' after covering, chosen $>$6 hr so the active deposit was in secular equilibrium with AcX. The extrapolation was accurate to only $\simeq$0·01 of A_N because of the small counting rates of freshly covered highly emanating samples and because the growth curve approximated a straight line only for about the first 3 min. Calculations of the shape of the growth curve were made, and the following equation was derived (see appendix) relating the emanating power E to the activity A measured at time t after covering.

$$E = \frac{1 - A/A_N}{H} \tag{5}$$

The constant H, the correction for growth, is a function of t, the known decay constants of AcX and its descendants, and the counting efficiency F of AcB relative to AcC″ (see appendix).

If the cover plus counter window were $\simeq$10 mg/cm², which was sufficient to stop the alpha particles from AcX, An, and AcA, it was found that some additional radiation from one or more of these nuclides contributed $\simeq$7 per cent of the measured equilibrium activity (A_N). An aluminium absorption curve taken on a highly emanating sample over which a current of air was passed showed this component to be soft (half-thickness $\simeq$9 mg/cm², effective range $\simeq$70 mg/cm²). Therefore, counting was done through 80 mg/cm² of aluminium.

The counting efficiency F of AcB relative to AcC″ for the counting conditions used (80 mg/cm² aluminium absorber, 10–20 mg/cm² of barium-stearate sample) was estimated to be 0·8 from consideration of the half-thickness values[11] for the radiations emitted.[12]

AcB—β^-: 1·39 MeV ($\simeq$80%), 0·5 MeV ($\sim$20%); γ: 0·06–0·83 MeV.
AcC″—β^-: 1·44 MeV.

Data from a typical experiment are given in Table 1. The data for the shortest times are the most reliable in spite of poor counting statistics because little correction for growth was necessary. Evidence that the choice of $F = 0{\cdot}8$ was a reasonably good one is the agreement of the average and initial emanating-power values and the lack of drift in the values with time. For values of F differing much from 0·8, the agreement was less good and a drift with time appeared. This is illustrated by the values of E calculated for $F = 0{\cdot}6$ and $F = 1{\cdot}0$.

This calculated method of extrapolation using equation (5) was estimated to give a precision of $\pm$0·005 in E, and the difference in two measurements was believed reliable to this figure. However, the emanating-power values so obtained were, within this uncertainty, only lower limits because of the probable contribution to A of radiations from AcX, An, and AcA not absorbed by 80 mg/cm² of aluminium. That there was still some small contribution from these nuclides was evidenced by the fact that for one sample, measured alternatively through two absorbers, an increase of absorber to 210 mg/cm², which reduced the beta intensity by a factor of 4·6, decreased the calculated emanating power from 0·990 to 0·970. This decrease indicates that the radiations from AcX, An and AcA penetrating 80 mg/cm² of aluminium were absorbed less by additional aluminium than the beta particles from AcB and AcC″ and, therefore, made a larger contribution to the A measured through the larger absorber.

[11] D. W. Engelkemeir, *Radiochemical Studies: The Fission Products* (Edited by C. D. Coryell and N. Sugarman) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 18. McGraw-Hill, New York (1951).
[12] J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. mod. Phys.* **25**, 469 (1953).

TABLE 1.—EMANATING POWER OF BARIUM STEARATE DETERMINED BY THE COVERED METHOD
(Preparation B, 11 mg/cm², No. 41H filter paper cover, in large evacuated desiccator, pressure ≤0·3 mm Hg, A_N = 11,000 counts/min)

t (min)	A/A_N(*)	H ($F = 0·8$)	E ($F = 0·8$)	E ($F = 0·6$)	E ($F = 1·0$)
1·00	0·0160	0·9915	0·922 ± 0·002†	0·991	0·993
2·25	0·0255	0·9804	0·994 ± 0·003	0·991	0·996
3·50	0·0281	0·9687	1·003 ± 0·002	0·999	1·007
5·50	0·0564	0·9483	0·995 ± 0·003	0·989	1·000
7·50	0·0887	0·9251	0·985 ± 0·003	0·977	0·991
9·50	0·1074	0·9004	0·991 ± 0·004	0·982	0·994
11·50	0·1315	0·8741	0·994 ± 0·004	0·983	1·002
		Average: 0·993		0·987	0·998

* A determined from 1 min counts except for 2·25 min point which was a 0·5 min count.
† Standard deviation from counting data.

Back-deposit effect

During the course of this investigation evidence was found that some of the active deposit formed from actinon which had escaped from an emanating barium stearate sample was deposited back on the sample. This contamination resulted in low values for the measured emanating power. The back-deposit effect was thought to be due to decay of a portion of the escaped actinon atoms in the vicinity of the sample before they could diffuse or be swept away. The effect was minimized by placing an emanating sample in a stream of air or by covering the sample with filter paper through which actinon readily diffused, but which caught any back deposit. The velocity of the air stream was limited because the powdered barium stearate was easily blown. Covering a sample with filter paper was simpler and more effective as shown in Table 2.

Solutions

The lead-sulphide method of measurement was modified by use of two identical solutions, one kept under non-emanating conditions and the other under the emanating conditions of interest (e.g., swept with air at 95°C) for 5 hr. For actinon, equation (4) with $t' = 0$ was applicable, A and A'

TABLE 2.—BACK-DEPOSIT EFFECT FROM BARIUM STEARATE EMANATING An FROM A THIN (<≃1 mg/cm²) LAYER

Conditions	Method of measurement	E
Standing in room air	PbS	0·92, 0·95
In hood air stream	covered	0·975
Between two pieces of No. 41H filter paper in room air	PbS	1·00, 0·99*
Between two pieces of No. 41H filter paper in room air	PbS	0·991, 0·997*
Between two pieces of No. 41H filter paper in room air	covered	0·987*

* Preparation B (used in the cumulative yield measurements[1]).

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being the activities of the PbS samples from the emanating and non-emanating solutions, respectively, and t being the time interval ($\simeq$6 min) between the cessation of sweeping and the mean time of the PbS filtration.

For thoron, transient equilibrium was not established in 5 hr, and it was not convenient to maintain the emanating conditions for the four days that would have been required. Therefore, before an experiment, 10·6 hr ThB (^{212}Pb) and 60·5 min ThC (^{212}Bi) were removed by two lead-sulphide precipitations, and the H_2S was expelled by boiling. Two equal aliquots were taken; one was stoppered and cooled (non-emanating solution), and the other was maintained at the desired conditions of temperature and gas sweeping. After 5 hr PbS was precipitated from each solution and the decay of ThB with its daughters in transient equilibrium was followed. Equation (1) was applicable, A_E and A_N being the activities of the PbS from the emanating and non-emanating solutions, respectively, each corrected for growth of ThB during the $\simeq$10 min period between the last PbS purification step and the placing of the aliquots under desired conditions for emanation. During this $\simeq$10 min period $\simeq$1 per cent of the equilibrium growth occurred, and since $\simeq$25 per cent of the equilibrium growth occurred during the 5 hr standing period, the maximum correction was 4 per cent of A_N. Actually a correction nearer 3 per cent of A_N was used, since it was estimated that 30 per cent of the Tn escaped under the conditions that existed during the 10 min period. In any case the correction was small and caused an estimated error in E of only about $\pm$0·01.

A summary of the data obtained is given in Table 3. As mentioned in the introduction, the experiments were of a preliminary nature and were not continued because barium stearate appeared to be more promising than the solutions as an efficient emanator. The near equivalence, under the best conditions, of the emanating powers for 51·5 sec Tn and 3·9 sec An suggests that a small portion of the solution was not swept effectively and that little of either isotope escaped from this portion. Such a region through which bubbles did not pass was observed near the bottom edges of the beaker. It seems probable that more efficient sweeping in a better designed apparatus would remove most of the thoron and actinon, but only at temperatures near 100°C.

TABLE 3.—EMANATING POWER OF SWEPT AQUEOUS SOLUTIONS
(50 ml of solution, 0·2 M in HCl, in 150 ml beaker)

Sweeping conditions	°C	E(Tn)	E(An)
No sweeping	98	0·26	—
Natural boiling	100	0·76	—
Air bubbles from 6 mm tube	95	0·81	—
Air bubbles from gas-dispersion tube*	95	0·90	—
Air bubbles from 2 gas-dispersion tubes*	22	0·71	0·55
Air bubbles from 2 gas-dispersion tubes*	50	0·81	—
Air bubbles from 2 gas-dispersion tubes*	75	0·87	—
Air bubbles from 2 gas-dispersion tubes*	95	0·93	$\simeq$0·9

* Gas-dispersion tube consisted of a fritted cylinder 2·5 cm long and 7 mm in diameter. The connecting tube was bent at a 90° angle so the axis of the cylinder could be placed parallel to the bottom of the beaker.

RESULTS

Thickness

As shown in Table 2 barium stearate in very thin layers emanates $\geqslant$99 per cent of the actinon. However, thicker layers were necessary to stop recoiling fission fragments, so emanating power as a function of thickness was studied. The results are summarized in Fig. 2. The points represent experimental values determined under various conditions explained in the legend. The curves are theoretical for escape of actinon from a stagnant column of air open only at one end at which the concentration of actinon is zero. The curves E_1 and E_2 are, respectively, for the

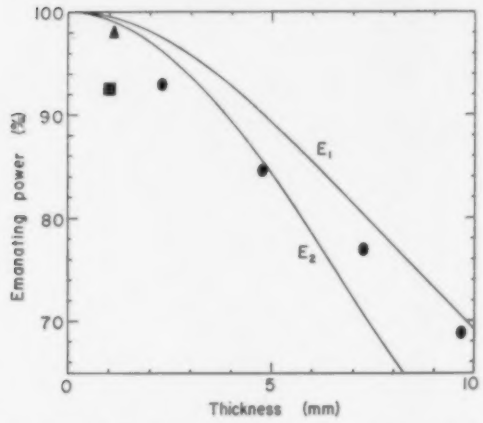

FIG. 2.—Emanating-power of barium stearate for An vs. thickness. Bulk density of powder was $\simeq 0{\cdot}1$ g/cm³. Cylinders closed at one end were filled with powder.
● exposed to air currents of the room.
▲ surface swept by air stream.
■ covered with No. 41H paper in closed desiccator at atmospheric pressure.
E_1 and E_2 are theoretical curves for emanation from a column of air [see equations (6) and (7)].

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situations in which actinon is formed (1) uniformly throughout the column volume, and (2) at the bottom of the column only.

$$E_1 = \frac{\tanh\,[(\lambda/D)^{1/2}a]}{(\lambda/D)^{1/2}a} = \frac{\tanh\,(1{\cdot}21\,a)}{1{\cdot}21\,a} \tag{6}$$

$$E_2 = \frac{1}{\cosh\,[(\lambda/D)^{1/2}a]} = \frac{1}{\cosh\,(1{\cdot}21\,a)}. \tag{7}$$

In the above equations, derived in the appendix, a is the height of the column (in mm) λ is the decay constant of actinon, and D is the diffusion coefficient of actinon in air, taken to be 0·120 cm²/sec, the value measured[13] at 760 mm Hg and 15°C.

As can be seen from Fig. 2 all of the experimental points fall below the E_1 curve, the upper limit of emanating-power for thick samples in air. The E_2 curve approximates the situation that would exist if recoil fragments were stopped in thick samples. The highest emanating power obtained was 98 per cent for an 11 mg/cm² (1 mm) sample swept by a stream of air. The emanating-power was only 93 per cent for a similar sample that was not swept but enclosed in a large volume of stagnant air and protected from back-deposit by filter paper.

The normal bulk density of the powdered barium stearate was $\simeq 0{\cdot}1$ g/cm³, but as can be seen from Table 4 no appreciable change in emanating-power was caused by moderate compression. Apparently the smaller thickness was offset by the smaller pore size, so the rate of diffusion from the air between the powder grains was not changed significantly.

Pressure

Since the low emanating power values ($<0{\cdot}99$) for thick samples was obviously due to slow diffusion of actinon from the air space between the powder grains, not from the grains themselves, the effect of air pressure on emanating power was studied.

[13] W. HIRST and W. HARRISON, *Proc. roy. Soc.* **A 169,** 573 (1939).

As expected and shown in Table 5, the emanating power values approached unity at low pressures.

TABLE 4.—EFFECT OF COMPRESSION ON EMANATING POWER
(11 mg/cm² of barium stearate emanating An in stream of air at atmospheric pressure, covered method of measurement)

Bulk density, g/cm³	E
0·11	0·979
0·23	0·983
0·42	0·977

TABLE 5.—EFFECT OF PRESSURE ON EMANATING POWER
(≃10 mg/cm² of barium stearate (prep. B) emanating An in a large desiccator; sample covered with No. 41H filter paper; covered method of measurement)

Pressure, (mm Hg)	E
760	0·928
76	0·983
7·5	0·992, 0·995*
<0·3	0·993, 0·995*, 0·993†

* In addition to the No. 41H filter-paper cover the sample was covered with ≃17 mg/cm² of inactive barium stearate (prep. B′) in which <0·5 per cent of the An decayed in passing through. Also <0·5 per cent of the An decayed in passing through the filter paper cover.

† Free space above the sample was limited to 36·5 ml (≃200 times the sample volume).

DISCUSSION

The practical objective of the investigation, the finding of conditions for the efficient removal of short-lived inert gases from a condensed phase, has been achieved. It has been shown that ⩾99 per cent of the 3·9 sec actinon escapes from the powder grains of barium stearate, and at low pressures (⩽7·5 mm Hg) ⩾ 99 per cent of the actinon escapes from a layer of barium stearate powder ≃10 mg/cm² thick. Also, it has been shown that no appreciable (<0·5 per cent) decay of actinon occurs in diffusing through a layer of barium stearate powder ≃17 mg/cm². Therefore, it was possible, as described in the preceding paper,[1] to determine the fractional cumulative yields of the short-lived krypton and xenon fission products.

It is of interest to understand why the actinon escapes so efficiently from solid barium stearate. The mean life of the actinon atoms in the grains must be ⩽0·06 sec for ⩽1 per cent of them to decay in the grains. Since FLÜGGE and ZIMENS[14] have shown that the emanating power due to direct recoil must be small (<1 per cent) for powders of any grain size, the escape mechanism must involve diffusion, either through the normal lattice material or from recoil pockets (indirect recoil). The emanating power due to diffusion E_D, derived by FLÜGGE and ZIMENS[14] for grains

[14] S. FLÜGGE and K. E. ZIMENS, *Z. phys. Chem.* B **42**, 179 (1939).

of such a size that there is very little escape by recoil, is

$$E_D = \frac{3}{y}\left(\coth y - \frac{1}{y}\right); \quad y = r(\lambda/D)^{\frac{1}{2}} \tag{8}$$

in which r is the radius of the grains (of assumed spherical shape), λ is the decay constant of the inert gas, and D is the diffusion coefficient of the inert gas in the solid material. Taking $D = 10^{-9}$ cm²/sec, as calculated from the measurements of GREGORY and MOORBATH[4] on the emanating power of barium stearate for 51·5 sec thoron as a function of temperature, r is $\leqslant 3 \times 10^{-5}$ cm. This dimension is for the microcrystals, many of which compose a powder grain of much larger dimensions ($\simeq 10^{-2}$ cm). The space between the microcrystals must be relatively large to afford the ready passage of the inert gas from the grain. This is strikingly shown in the appendix of the preceding paper[1] by the 99·2 per cent emanating power of a large ($\simeq 0{\cdot}5$ cm) lump in vacuum.

The diffusion coefficient of 10^{-9} cm²/sec is large for diffusion of radon in solids (for example, D for diffusion in barium nitrate[15] is $\simeq 10^{-18}$ cm²/sec), and GREGORY and MOORBATH[4] propose that the diffusion is by numerous defects in the lattice. However, the coefficient is small compared to those for diffusion of radon in water[16] ($\simeq 10^{-5}$ cm²/sec) and air[13] ($\sim 0{\cdot}1$ cm²/sec at 1 atm). The more efficient escape of actinon from barium stearate than from gas-swept aqueous solution must be due to the very short diffusion distance ($\leqslant 3 \times 10^{-5}$ cm) in the barium stearate itself, most of the diffusion distance being in air or vacuum between the microcrystals composing the grains and between the grains themselves. In water, since the rate of actinon diffusion is much larger than in the barium stearate lattice, the diffusion distance must be very much greater.

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APPENDIX

Growth of AcB and AcC″ after the emanating power of an AcX sample is cut to zero

Consider a sample of AcX that has emanated An with an emanating power E for a period of time sufficiently long for secular equilibrium to be established, i.e., $\lambda_2 N_2 = \lambda_3 N_3 = \lambda_4 N_4 = (1 - E)\lambda_1 N_1$, the subscripts 1, 2, 3, and 4 referring to AcX, AcB, AcC, and AcC″, respectively (see Fig. 1). At time $t = 0$ the sample is converted to a non-emanating state ($E = 0$), e.g., by being covered with a material that is impervious to actinon. The beta activities A_2 and A_4 of AcB and AcC″, respectively, at time t after the conversion are given by the following equations, which are applicable for times much shorter than the half-life of AcX ($t \ll 1/\lambda_1$). The symbol C represents counting efficiency, and N_1^0 represents the number of AcX atoms present at $t = 0$.

$$A_2 = C_2\lambda_2 N_2 = EC_2\lambda_1 N_1^0(1 - e^{-\lambda_2 t}) + (1 - E)C_2\lambda_1 N_1^0 = C_2\lambda_1 N_1^0(1 - Ee^{-\lambda_2 t}) \tag{9}$$

$$A_4 = C_4\lambda_4 N_4 = EC_4\lambda_1 N_1^0(1 - J) + (1 - E)C_4\lambda_1 N_1^0 = C_4\lambda_1 N_1^0(1 - EJ) \tag{10}$$

$$J = \frac{\lambda_2\lambda_4 e^{-\lambda_2 t}}{(\lambda_3 - \lambda_2)(\lambda_4 - \lambda_2)} + \frac{\lambda_2\lambda_4 e^{-\lambda_3 t}}{(\lambda_2 - \lambda_3)(\lambda_4 - \lambda_3)} + \frac{\lambda_2\lambda_3 e^{-\lambda_4 t}}{(\lambda_2 - \lambda_4)(\lambda_3 - \lambda_4)}. \tag{11}$$

Let $F = C_2/C_4$ and $A = A_2 + A_4$. Then the equilibrium activity A_N at $t = 0$ of AcB plus AcC″ under non-emanating conditions is $A_N = (1 + F)C_4\lambda_1 N_1^0$, and

$$\frac{A}{A_N} = \frac{F\lambda_2 N_2 + \lambda_4 N_4}{(1 + F)\lambda_1 N_1^0} = \frac{F(1 - Ee^{-\lambda_2 t}) + (1 - EJ)}{1 + F} = 1 - \frac{E(Fe^{-\lambda_2 t} + J)}{1 + F} = 1 - EH \tag{12}$$

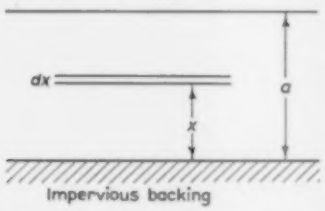
$$E = \frac{1 - A/A_N}{H} \tag{13}$$

$$H = \frac{Fe^{-\lambda_2 t} + J}{1 + F} = \frac{(F + 1{\cdot}2252)e^{-\lambda_2 t} + 0{\cdot}0529e^{-\lambda_3 t} - 0{\cdot}2781e^{-\lambda_4 t}}{1 + F}. \tag{14}$$

[15] F. STRASSMANN, *Z. phys. Chem.* B **26**, 353 (1934).
[16] E. RONA, *Z. phys. Chem.* **92**, 213 (1916–18).

Emanating power of thick samples

Only samples with dimensions very much greater than the recoil range will be considered so recoil of the inert gas from the sample may be neglected. The concentration of inert gas above



the sample is taken to be zero. GREGORY, HILL and MOORBATH[17] gave for the emanating power of layer dx

$$E = \frac{(D/\lambda)^{\frac{1}{2}} \cosh [(\lambda/D)^{\frac{1}{2}} x] \sinh [(\lambda/D)^{\frac{1}{2}} R]}{R \cosh [(\lambda/D)^{\frac{1}{2}} a]} \tag{15}$$

in which D is the diffusion coefficient of the inert gas in the material, λ is the decay constant of the inert gas, and R is its recoil range. For values of D sufficiently large that $(\lambda/D)^{\frac{1}{2}} R \ll 1$,

$$\sinh [(\lambda/D)^{\frac{1}{2}} R] = (\lambda/D)^{\frac{1}{2}} R$$

and

$$E = \frac{\cosh [(\lambda/D)^{\frac{1}{2}} x]}{\cosh [(\lambda/D)^{\frac{1}{2}} a]} . \tag{16}$$

As x approaches zero, i.e., the inert gas is formed only near the bottom of the sample (but does not recoil into the backing),

$$E_2 = \frac{1}{\cosh [(\lambda/D)^{\frac{1}{2}} a]} . \tag{17}$$

If the inert gas is formed uniformly throughout the sample

$$E_1 = \frac{\int_0^a \frac{\cosh [(\lambda/D)^{\frac{1}{2}} x]}{\cosh [(\lambda/D)^{\frac{1}{2}} a]} dx}{\int_0^a dx} = \frac{\tanh [(\lambda/D)^{\frac{1}{2}} a]}{(\lambda/D)^{\frac{1}{2}} a} . \tag{18}$$

[17] J. N. GREGORY, J. F. HILL and S. MOORBATH, *Trans. Faraday Soc.* **48**, 643 (1952).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 288–294. Pergamon Press Ltd., London

CHEMICAL EFFECTS IN FISSION PRODUCT RECOIL—III

THE DECOMPOSITION OF POTASSIUM NITRATE

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Abstract—The effect of the recoil of fission products from uranium foils into an adjacent layer of potassium nitrate has been investigated. Under these conditions about 10·5 nitrite ions are formed per 100 eV of recoil energy absorbed. This is considerably greater than the values observed for other forms of radiation and the reasons for this are discussed.

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INTRODUCTION

THE chemical effects of fission recoils may be studied in solids in a single phase, or in a two phase system. In the first the fissile atoms may be combined in a salt which is susceptible to radiation damage, such as uranyl iodate[1] or oxalate[2,3] and here the whole of the fission fragment energy is expected to be adsorbed in the material investigated. The number of solid materials which may be studied in this way is, however, limited to compounds, or mixed crystals, of the heavy elements. In the second system, for which a wider variety of materials may be used, the fissile atoms may be in one phase, while the material investigated is in another, and in the fission process the fragments recoil from the one phase to the other. For instance several studies have been made in which uranium oxide was mixed with detonating materials[4] with graphite[5] or with potassium iodate.[6] In these experiments, it was necessary to estimate the manner in which the energy distributes itself between the two phases, and this is open to a great deal of uncertainty where mixtures of powders are involved. In the following study two phases adjoin at a flat surface, and it has been shown previously that the energy distribution may be approximately calculated[6] since fission fragments recoil through matter along linear tracks.

Smooth uranium metal foil was used in most of the experiments as the source of the recoils. The recoil range in uranium is of the order 7 μ[7] and an irregularity of this depth would be visible in the surface of the uranium. For this reason foil which appeared smooth was considered to be sufficiently flat. The target material was pressed into a smooth surfaced disk which was held flat against the foil by light spring loading.

Various materials were considered for the target. Some experiments were tried with sodium azide, but the accurate measurement of the nitrogen evolved after

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[1] D. HALL, *J. inorg. nucl. Chem.* **6**, 3 (1958).
[2] I. F. CROALL and D. HALL, To be published.
[3] J. WRIGHT and D. A. YOUNG, To be published.
[4] F. P. BOWDEN and K. SINGH, *Proc. roy. Soc.* A **227**, 22 (1955).
[5] D. F. SANGSTER and J. WRIGHT, *Nature, Lond.* **170**, 368 (1952).
[6] G. N. WALTON and I. F. CROALL, *J. inorg. nucl. Chem.* **1**, 149 (1955).
[7] E. SEGRÈ and C. WIEGAND, *Phys. Rev.* **70**, 808 (1946).

dissolution of the irradiated salt in water proved to be too elaborate for a systematic study. Potassium nitrate was chosen as a suitable material. The main radiation decomposition product is the nitrite ion,[8,9] and rapid, sensitive, and accurate, methods are available for measuring it. The assumption was made that the nitrite ion was also the main decomposition product in fission recoil, and that it could be used to measure the amount of decomposition in the nitrate.

The number of fission fragments entering the potassium nitrate phase was found by measuring the quantity of two representative fission products of well established fission yield. Strontium-89 was chosen to represent the light fragments, and barium-140 the heavy fragments. These fission products have no complexities in their decay chains and they readily exchange with carrier solutions, so that their analysis is not open to large uncertainties.

EXPERIMENTAL

"Analar" grade potassium nitrate, dried and finely ground, was pressed in a die under pressures of over 1000 lb/in^2 into thin disks with smooth surfaces, diameter 0·5 in., mass 50 to 100 mg. Those of mass greater than 70 mg were of sufficient mechanical strength to withstand normal handling, but lighter disks became progressively more fragile. They were placed between similar disks cut from uranium foil, and the sandwich was held in a steel clip between aluminium discs. The assembly was sealed into an evacuated glass capsule and irradiated in BEPO, in a position of rated flux $1{\cdot}4 \times 10^{12}$ n cm^{-2} sec^{-1}. The relative neutron doses received by the various samples were estimated by affixing to each capsule a monitor of cobalt wire, which was subsequently counted.

After several days the capsules were opened and the potassium nitrate dissolved in a barium-strontium nitrate carrier solution. An aliquot of this solution was analysed for nitrite by SHINN's method[10] in which sulphanilamide is added to the acidified solution, and the resulting diazo compound coupled with *N*-(1-naphthyl)-ethylenediamine dihydrochloride. The colour so produced was measured with a Hilger "Spekker" absorptiometer previously calibrated, using a filter which transmitted in the region 0·50 to 0·55. A further aliquot was analysed radiochemically for ^{89}Sr and ^{140}Ba by the following procedure. Barium and strontium nitrates were precipitated with fuming nitric acid, then dissolved in water and the solution scavenged twice with ferric hydroxide. $BaCl_2.H_2O$ was precipitated with HCl–ether reagent, centrifuged, and dissolved in lanthanum–strontium carrier. It was reprecipitated with HCl–ether, redissolved in water, and after repeating this process again the barium was finally precipitated as the sulphate. The original HCl–ether filtrate was evaporated to dryness, and redissolved in the minimum of very dilute hydrochloric acid. The strontium was then purified by elution with 7·5 per cent ammonium citrate from a column of Zeocarb-225 resin, and precipitated as sulphate from 50 per cent alcoholic solution. The precipitate was mounted on filter paper circles, weighed and counted in an internal source, 2π geometry proportional counter. The corrections for self absorption, scattering and geometrical efficiency given by CUNINGHAME *et al.*[11] for this counter were then applied, and the disintegration rates thus obtained further corrected for decay and chemical yield. The ^{140}Ba samples were not counted until equilibrium had been established with ^{140}La, and the lanthanum contribution was allowed for. Radiochemical purity was checked by plotting aluminium absorption curves, and by following the decay of selected barium samples.

Uranium foils of thickness 95, 150 and 700 mg cm^{-2} were used, and in one experiment an evenly deposited layer of uranium oxide, thickness 3 mg cm^{-2}, on a platinum backing. Foils of thickness 20 to 35 mg cm^{-2} proved unsatisfactory, as they disintegrated under irradiation, which made clean separation of the nitrate impossible.

The decomposition of potassium nitrate under pile irradiation was determined in a similar series of experiments, in which all the relevant details were reproduced.

[8] G. HENNIG, R. LEES and M. S. MATHIESON, *J. chem. Phys.* **21**, 665 (1953).
[9] H. G. HEAL and J. CUNNINGHAM, Private communication; J. CUNNINGHAM, Thesis presented at Queen's University, Belfast (1957).
[10] M. B. SHINN, *Industr. Engng. Chem. (Anal.)* **13**, 33 (1941).
[11] J. G. CUNINGHAME, M. L. SIZELAND and H. H. WILLIS, AERE C/R 1646 (1955); AERE C/R 2054 (1957).

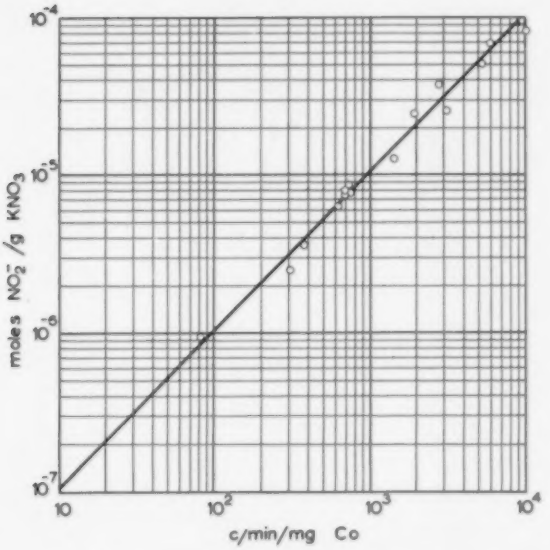

FIG. 1.—Decomposition due to the background pile radiation.

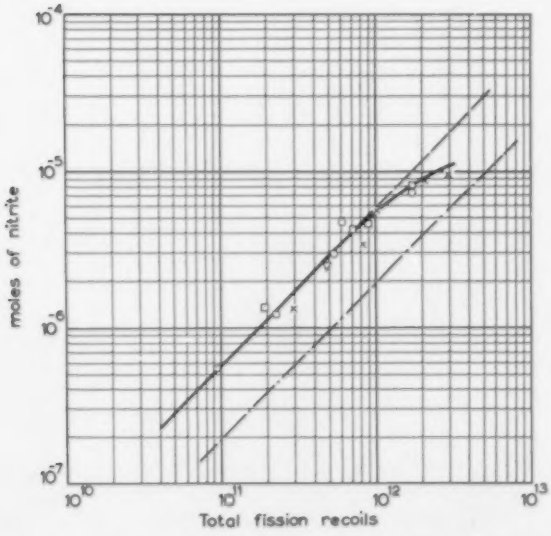

FIG. 2.—Decomposition due to recoiling fission fragments.
□ Uranium foil thickness 700 mg cm^{-2}.
○ Uranium foil thickness 150 mg cm^{-2}.
× Uranium foil thickness 95 mg cm^{-2}.
△ Uranium oxide thickness 3 mg cm^{-2}.
The magnitude of the average pile background effect is shown by the line — — — —.

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RESULTS

The fission yields of masses 89 and 140 in the thermal neutron fission of ^{233}U are 4·8 and 6·3 respectively,[12] and their ratio is 0·76. For the recoil atoms this ratio was found to be 1·06, which is 1·39 times the fission yield ratio. The amount of fission products escaping by recoil from an effectively infinitely thick layer is directly proportional to the range,[6] and it follows that the range in uranium of mass 89 is 1·39 times that of mass 140. This may be compared with the value of 1·36 in aluminium[13] and 1·33 for plutonium fission fragments in air.[14] The total number of recoils was estimated from the mean of the two values obtained assuming the normal fission yeilds.

In Fig. 1 the decomposition per gram of KNO_3 due to pile radiation is plotted against the neutron dose, as measured by the cobalt monitors. In Fig. 2 the amount of nitrite found in the recoil experiments, with the pile background effect subtracted, is plotted against the number of recoils. On the same figure the magnitude of the background for the same neutron dose is shown, assuming a 75 mg sample. In both cases a marked scatter of points is apparent, and this was found to be due to the quality of the disks. It was found subsequently that if the pressed disks and crystals of the batch from which they were prepared were irradiated simultaneously, the disks suffered only about half the decomposition shown by the crystals. The compacting of macro crystals to form the microcrystalline disks appeared to decrease the ease with which the nitrate ions dissociate. No attempt was made to produce the disks under precicely the same conditions of pressure and time of pressing, and they may vary in this respect. Another reason for the scatter in points is that the cobalt monitors measure only the thermal neutron and not the total radiation dose, and that the presence of other samples in the irradiation stringer can produce considerable local fluctuation in the quality of the pile radiation. The background effects in these experiments are large, and such inaccuracies in their estimation could produce the observed scatter of the final results.

Nevertheless, the relationship between decomposition and the number of recoils may be seen to be roughly linear, with a falling off in linearity at high dose. Assuming the range of fission fragments in potassium nitrate to be 3·7 mg cm^{-2} (as in aluminium[13]), the onset of this fall off in linearity corresponds to an average of 5 per cent decomposition within the affected region, although nearer the surface the percentage decomposition will in fact be much greater. From the linear region of Fig. 2 the yield of nitrite was determined as $5{\cdot}6 \times 10^{-18}$ moles per recoil fragment.

Recoil fragments can emerge only from the outer 4·6 mg cm^{-2} of a massive uranium foil,[7] but the more penetrating radiations accompanying fission throughout the uranium would be expected to cause some dependence of the nitrate yield on the foil thickness. However it may be seen from Fig. 2 that any such dependence is of no greater order than the experimental uncertainty. When an aluminium foil of thickness 15 mg cm^{-2} (i.e. sufficient to absorb all recoil fragments) was placed between the uranium and the nitrate disc the decomposition observed was greater than the normal background level, and it was deduced that as much as 15 per cent of the above yield may be due to fission effects other than recoil. The true yield for each recoil is then $4{\cdot}8 \times 10^{-18}$ moles. This reduction was not apparent in the experiment using the thin film of uranium oxide, where it is possible that it was compensated by a reduction in self absorption of the fission fragment energy. The effect of very thin films using enriched uranium, where there is almost no self-absorption, forms the subject of a further investigation.

DISCUSSION

In these experiments extensive planar surfaces of fissile and target materials were in contact. The mass of air or gas which could be trapped between the two surfaces would have negligible stopping power compared with the mass of material in the disks. The range of fragments in air is of the order 2 cm and the solid angle subtended by one disk from a point on the other could not be significantly less than 2π. The conditions therefore correspond to those for which WALTON and CROALL[6] calculated that on the average, one third of the recoil energy of fragments originating

[12] E. P. STEINBERG and L. E. GLENDENIN, *International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, Paper P/614. United Nations (1956).

[13] B. FINKLE, E. J. HOAGLAND, S. KATCOFF and N. SUGARMAN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 463. McGraw-Hill, New York (1951).

[14] S. KATCOFF, J. A. MISKEL and C. W. STANLEY, *Phys. Rev.* **74**, 631 (1948).

in an effectively infinitely thick layer of fissile material would be expended in the target phase. Assuming 81 MeV as the initial mean kinetic energy per fragment, and allowing for 15 per cent decomposition due to fission effects other than recoil, the G factor is then 10·5 nitrite ions formed per 100 eV absorbed. The pressed disks used in this work were shown to be less susceptible to decomposition (by pile radiation) than the macrocrystals, and if their use has had any effect on the observed recoil G factor it must have been to diminish it rather than to increase it.

ERSCHLER and LAPTEON[15] observed an evaporation effect from irradiated uranium which was attributed to atoms carried out from the surface of the fissile phase by the recoiling fission fragments. For a metallic surface they report that about 1000 atoms evaporate for every fission recoil. The proportion of the fission product atoms in the uranium for our irradiations is about 1 in 10^6 and this evaporation effect would not significantly alter the number of fission fragments reaching the nitrate phase. If there was any significant effect of this nature it would diminish the calculated G factor, rather than increase it. It is concluded therefore that the true G factor for nitrate formation by recoil must be at least 10·5.

HENNIG, LEES and MATHIESON[8] report that electron irradiation and pile irradiation in which energy is deposited by γ-rays and fast neutrons, produce 0·72 to 0·92 moles of oxygen for every 100 eV absorbed. The same authors report that two moles of nitrite are formed for every mole of oxygen so that the above values correspond to G values for nitrite formation of 1·4 to 1·8. HEAL and CUNNINGHAM[9] have shown that for X-ray irradiation the G value varies in a complex manner from about 1·7 at $-180°$C to about 3·2 at $+200°$C. All these values are less by a large factor than the value found for fission recoil.

A recent study by WRIGHT and YOUNG[3] has also shown that fission recoils are more efficient at causing decomposition of uranyl oxalate than γ-radiation.

An important difference between recoiling fission fragments and γ-irradiation is that the former loses an appreciable fraction of its energy by producing atom displacements in a crystal lattice, whereas γ-radiation is absorbed mainly by electronic excitation and ionization. Fast neutrons also lose a large fraction of their energy in causing displacements and HENNIG, LEES and MATHIESON[8] investigated this effect. They irradiated potassium nitrate with electrons calculated to be below the threshold energy necessary to cause displacements, and found that the decomposition was about the same as that found for pile irradiations, and they concluded that there was no evidence that fast neutron displacement effects caused additional decomposition.

PRINGSHEIM[16] studied the absorption spectra of sodium nitrate which had been irradiated in various ways. He found that in crystals irradiated in a reactor the amount of nitrite formed relative to colour centres was much higher than in crystals irradiated with X-rays. This would appear to suggest that nitrite formation was due to atom displacements, but it was also shown that with X-ray irradiation at low temperatures ($-190°$C) the ratio of nitrite to colour centres was again high. It was concluded that the alteration in the ratio was due to bleaching of the colour centres at the higher temperatures at which the pile radiations were conducted, and that there was again no evidence that displacements were especially important in causing decomposition.

[15] B. V. ERSCHLER and F. S. LAPTEON, *J. nucl. Energy* **4**, 471 (1957).
[16] P. PRINGSHEIM, *J. chem. Phys.* **23**, 369 (1955).

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ANDERSON[17] has shown very recently that the energy deposition by fast neutrons, for materials having atomic numbers in the region of aluminium, placed in the moderator of a reactor core, is only a very small fraction (1·4 per cent) of the energy deposited by γ-radiation. It is therefore unlikely that any fast neutron effect in the experiments by HENNIG *et al.* and by PRINGSHEIM would be observable.

From the theory of the displacement of atoms by moving particles, as reviewed by KINCHIN and PEASE,[18] it is possible to make a rough estimate of the number of atoms displaced by a recoiling fission fragment in potassium nitrate. Interaction is assumed to occur by Coulomb repulsion between nuclei only when the nuclei approach sufficiently closely and with sufficient energy for the electron screens of the two atoms to interpenetrate. For fission fragments all such collisions are expected to displace atoms and it may be calculated that the total number of displacements per fission fragment is about $8{\cdot}6 \times 10^4$. The observed value of the number of nitrate ions decomposed per fission fragment is $8{\cdot}2 \times 10^6$, which is two orders of magnitude greater than the number of displacements. This again suggests that the physical displacement of atoms is not the primary cause of the decomposition.

Another important difference between recoiling fission fragments and other forms of irradiation is that the energy is dissipated in a very small volume. Table 1 shows some values for the energy dissipated per unit length of the range for various radiations calculated from the estimated range in potassium nitrate.

TABLE 1.—DENSITY OF ENERGY DEPOSITION BY VARIOUS RADIATIONS IN POTASSIUM NITRATE

		MeV/cm
Fission fragments	(80 MeV)	$4{\cdot}5 \times 10^4$
α-particles	(5 MeV)	$1{\cdot}5 \times 10^3$
Electrons	(0·5 MeV)	4·0
γ-rays	(1 MeV)	(0·7)

As described by SEITZ[19] the track of fission fragments may be considered as a thermal spike in which the energy absorbed corresponds to a temperature of about 4000°C over a cylinder of length $1{\cdot}76 \times 10^{-3}$ cm and 100 Å diameter, in which the lattice bonding must be momentarily destroyed. The duration time is calculated to be of the order 10^{-11} sec. From our observations the total number of molecules decomposed along the track is $8{\cdot}6 \times 10^6$, and from the density of potassium nitrate this number of molecules would occupy a cylinder $1{\cdot}76 \times 10^{-3}$ cm long and 70 Å diameter. This is nearly as big as the calculated size of the thermal spike, so that nearly all neighbouring ions would be decomposed. In this situation it might be supposed that a large amount of recombination would occur and that the G factor for fission recoils would be particularly small.

HEAL and CUNNINGHAM[9] conclude from their detailed study of the X-ray decomposition of potassium nitrate that the most important factor in controlling the

[17] A. R. ANDERSON, Private communication.
[18] G. H. KINCHIN and R. S. PEASE, *Rep. Progr. Phys.* **18**, 1 (1955).
[19] F. SEITZ, *Disc. Faraday Soc.* **5**, 271 (1949).

decomposition is the ability of the oxygen atom released from an excited nitrate ion to escape from the lattice "cage" surrounding it.

The decomposition of a single nitrate ion to nitrite involves the release of an oxygen atom.

$$NO_3^- \rightarrow NO_2^- + O$$
$$2O \rightleftharpoons O_2$$

The heat of recombination of two oxygen atoms to form an oxygen molecule is, at ordinary temperatures, 59 kcal/mole, so that the back reaction between oxygen and nitrite ions is radically dependent upon whether the oxygen is in the atomic or molecular form. HEAL and CUNNINGHAM[9] found no evidence for a back reaction in the X-ray decomposition of potassium nitrate, but the kinetics over a wide range of temperature suggested that the concentration of molecular oxygen played an important part in determining the fraction of oxygen atoms which escaped the lattice "cage" effect.

In the conditions of the fission recoil track there can be very little "cage" effect, and the oxygen atoms would be expected to be free to move from the vicinity of the nitrite ion. If the duration of the spike is 10^{-11} sec there is sufficient time for the oxygen atom to move a few molecular diameters. Also, above 4000°C the oxygen atoms would remain dissociated, and could only associate to form oxygen molecules below this temperature. It may be estimated from the entropy and heat changes[20] in the reaction

$$\underset{\text{cryst}}{KNO_2} + \underset{\text{gas}}{O} \rightleftharpoons \underset{\text{cryst}}{KNO_3} \quad -\Delta H_{298^\circ} = 88{\cdot}5 \text{ kcal} \quad -\Delta S = 31{\cdot}3 \text{ cal/deg.}$$

that the oxygen atoms will not be expected to combine with nitrite above about 2500°C and so in the conditions of the thermal spike the oxygen atoms will combine with each other preferentially to combining with nitrite ions. Once the oxygen molecule has been formed there is a potential barrier of 20·7 kcal/mole preventing recombination with the nitrite.[21] In X-ray irradiation the nitrite ions and oxygen atoms are less likely to move appreciably from the site where they are formed, there is less likelihood of oxygen atoms meeting to form molecules, and as there is no evidence that oxygen atoms remain in the crystals after irradiation,[8,9] primary recombination is probable. It is suggested that this could account for the difference in G values between fission recoil and X-ray irradiation.

In comparing the G values for nitrate decomposition for a number of alkali and alkaline earth elements it has been concluded that the "free space" i.e. the space left after subtracting the volumes of the cation and anion from the molecular volume, determines the susceptibility to radiation decomposition.[8,9] It is further postulated[9] that this is because an oxygen atom can more readily escape its lattice "cage" when the "free space" in a molecule is large, or suitably orientated. On this interpretation, molecules at the surfaces of crystals might be more susceptible to decomposition than molecules in the interior of a crystal lattice. It is possible that this explains why the compressed disks of potassium nitrate used in our investigation of fission recoil effects were less susceptible to decomposition by pile irradiation than uncompressed crystals which would have a greater free surface area. In decomposition by fission recoil, where we have postulated that the "cage" effect is not operative, the compression of the crystals would not be expected to have so great an influence.

[20] *Selected Values of Thermodynamic Data*, NBS Circular 500 (1952).
[21] E. S. FREEMAN, *J. phys. Chem.* **60**, 1487 (1956).

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J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 295 to 302. Pergamon Press Ltd., London

LATTICE ENERGIES AND RELATED PROPERTIES DERIVED USING LYOTROPIC NUMBERS

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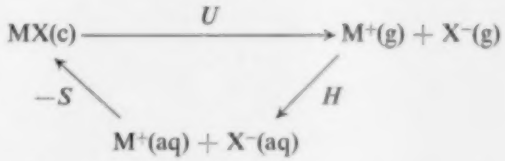
Abstract—The linear relationship between hydration heat and lyotropic number has been employed to obtain combined ion-hydration heats of alkali metal cations with the anions, nitrate, nitrite, perchlorate, chlorate, bromate, iodate and the thiocyanate. These values have been employed in conjunction with heat of solution data to derive lattice energies. Other magnitudes, which have been computed, include enthalpies of gaseous anions, anion hydration heats, and the electron affinities of NO_2, NO_3, ClO_3 and ClO_4. The fact that lyotropic numbers indicate different ionic field strengths is discussed.

THE lattice energy of a crystal MX is included in the thermodynamic cycle shown below,



The cycle is given in terms of enthalpies, and the symbols are defined by the following thermochemical equations:

$MX(c) = M^+(g) + X^-(g)$	$\Delta H_{298} = U$, lattice energy of MX.
$M^+(g) + X^-(g) + aq = M^+(aq) + X^-(aq)$	$\Delta H_{298} = H$, enthalpy of hydration of the two gaseous ions.
$MX(c) + aq = M^+(aq) + X^-(aq)$	$\Delta H_{298} = S$, standard enthalpy of solution of MX(c).

The changes in enthalpy must add up to zero; hence

$$U = -H + S \tag{1}$$

In the case of the alkali halides, values of lattice energy and heat of solution are well known and equation (1) may be used to evaluate the enthalpy of hydration of the gaseous ions. In Table 1 are shown values of H for the combined hydration heats of alkali and halide ions; the data are from LATIMER *et al.*[1] and have been derived using the quite reliable lattice energy values computed by HUGGINS[2] corrected to 298°K.[3]*

An empirical correlation between ion hydration heat and lyotropic number has

* In MORRIS[3] the value of I for potassium should be 100 kcal, and values of U for the potassium halides should be reduced by 2 kcal mole^{-1}.

[1] W. M. LATIMER, K. S. PITZER and C. M. SLANSKY, *J. chem. Phys.* **7**, 108 (1939).
[2] M. L. HUGGINS, *J. chem. Phys.* **5**, 143 (1937).
[3] D. F. C. MORRIS, *Acta Cryst.* **9**, 197 (1956).

TABLE 1.—COMBINED ENTHALPIES OF HYDRATION, H, OF ALKALI AND HALIDE IONS
[Values in kcal/g ion pair (298°K)]

	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	−243·8	−217·2	−198·4	−191·8	−184·6
Cl^-	−209·9	−183·3	−164·5	−157·9	−150·7
Br^-	−202·6	−176·0	−157·2	−150·6	−143·4
I^-	−193·3	−166·7	−147·9	−141·3	−134·1

been observed and substantiated.[4] The lyotropic number developed by BUCHNER, VOET and BRUINS,[4,5,6] is a quantitative expression of the position of an anion in the lyotropic (Hofmeister) series. If the data of Table 1 are plotted against the lyotropic numbers of the halide ions linear relationships are observed—Fig. 1. From values of

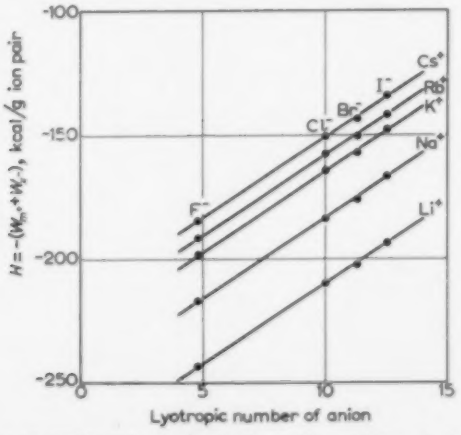


FIG. 1.—Dependence of combined ion-hydration heat, $H = -(W_{M^+} + W_{X^-})$, on lyotropic number.

the lyotropic numbers of other anions,[4] the combined heats of hydration of the anions with alkali metal cations may be estimated by interpolation. Heats of hydration obtained in this way, together with experimentally determined heats of solution, may then be employed to estimate lattice energies of alkali metal salts from equation (1). This procedure has been employed successfully by GRAY and WADDINGTON[7] in the determination of the lattice energies of azides. It is employed in the present paper for estimating the lattice energies of other compounds and the derivation of various thermochemical magnitudes not generally susceptible to direct measurement.

LATTICE ENERGIES OF SOME ALKALI METAL SALTS

Utilizing the lyotropic numbers listed in Table 2, the heats of hydration of alkali metal ions with iodate, bromate, nitrite, chlorate, nitrate, perchlorate and thiocyanate

[4] E. H. BUCHNER, *Kolloidzschr.* **75**, 1 (1936).
[5] A. VOET, *Chem. Rev.* **20**, 169 (1937).
[6] E. H. BUCHNER, A. VOET and E. M. BRUINS, *Proc. Acad. Sci. Amsterdam* **35**, 563 (1932).
[7] P. GRAY and T. C. WADDINGTON, *Proc. roy. Soc.* A **235**, 481 (1956).

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TABLE 2.—BUCHNER'S LYOTROPIC NUMBERS, N, FOR SOME ANIONS

Anion	N
F^-	4·8
IO_3^-	6·25
BrO_3^-	9·55
Cl^-	10
NO_3^-	10·2
ClO_3^-	10·65
Br^-	11·3
NO_3^-	11·6
ClO_4^-	11·8
I^-	12·5
CNS^-	13·25

TABLE 3.—HYDRATION HEATS, HEATS OF SOLUTION AND LATTICE ENERGIES FOR SOME ALKALI METAL COMPOUNDS

[Data are enthalpies in kcal (298°K)]

Compound	H	S^*	U
$LiNO_3$	−199·4	−0·647	198·8
$NaNO_3$(II)	−172·7	4.899	177·6
KNO_3	−154·2	8·348	162·5
$RbNO_3$(II)	−147·1	8·74	155·8
$CsNO_3$(II)	−140·2	9·51	149·7
$NaClO_3$	−178·8	4·95	183·8
$KClO_3$	−160·4	9·96	170·4
$RbClO_3$	−153·5	11·4	164·9
$NaClO_4$(II)	−171·4	3·49	174·9
$KClO_4$	−152·9	12·15	165·1
$RbClO_4$(II)	−145·9	13·57	159·5
$CsClO_4$	−138·9	13·26	152·2
$NaNO_2$(II)	−181·8	3·3	185·1
KNO_2	−163·3	3·3	166·6
KIO_3	−189·1	6·5	195·6
NaCNS	−161·8	1·63	163·4
KCNS	−142·9	5·82	148·7
RbCNS	−136·4	12·3	148·7

* Values for the heats of solution have been obtained from the compilation of ROSSINI *et al.*[6]

[6] F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE, *Selected Values of Chemical Thermodynamic Properties*. Circ. Nat. But. Stand. no. 500 (1952).

ions can be determined by interpolation. The lattice energies of crystalline compounds formed from the corresponding pairs of ions may then be derived using equation (1), if heat of solution data are available. Results obtained in this way are given in Table 3.

The consistency of the lattice energies listed in Table 3 can be tested by deriving the values of $\Delta H_f(X^-g)$, the enthalpies of the gaseous anions, from the equation,

$$\Delta H_f(X^-g) = U - \Delta H_f(M^+g) + \Delta H_f(MXc). \quad (2)$$

Table 4 summarizes the results. It can be seen that the degree of constancy of the $\Delta H_f(X^-g)$ values is satisfactory.

The only other calculations of lattice energies of compounds listed in Table 3 appear to be those of YATSIMIRSKII,[9] which have been made using the approximate equation of KAPUSTINSKII,[10]

$$U_0 = 287{\cdot}2\,\frac{\nu Z_1 Z_2}{r_1 + r_2}\left\{1 - \frac{0{\cdot}345}{r_1 + r_2}\right\} \text{ kcal.} \quad (3)$$

In this equation ν is the number of ions in the chemical molecule, Z_1 and Z_2 are the

TABLE 4.—CONSISTENCY OF DATA; INDEPENDENT VALUES OF $\Delta H_f(X^-g)$ DERIVED FROM DATA OF TABLE 3

Compound	U	$\Delta H_f(MXc)$‡	$\Delta H_f(M^+g)$†	$\Delta H_f(X^-g)$*
$LiNO_3$	198·8	−115·279	162·86	−79·4
$NaNO_3$(II)	177·6	−111·54	146·015	−80·0
KNO_3	162·5	−117·76	123·07	−78·3
$RbNO_3$(II)	155·8	−117·04	118·297	−79·5
$CsNO_3$(II)	149·7	−118·11	110·081	−78·5
$NaClO_3$	183·8	−85·73	146·015	−48·0
$KClO_3$	170·4	−93·50	123·07	−46·2
$RbClO_3$	164·9	−93·8	118·297	−47·2
$NaClO_4$(II)	174·9	−92·18	146·015	−63·3
$KClO_4$	165·1	−103·6	123·07	−61·6
$RbClO_4$(II)	159·5	−103·87	118·297	−62·7
$CsClO_4$	152·2	−103·86	110·081	−61·8
$NaNO_2$(II)	185·1	−85·9	146·015	−46·8
KNO_2	166·6	−88·5	123·07	−45·0
KIO_3	195·6	−121·5	123·07	−49·0
NaCNS	163·4	−41·73	146·015	−24·3
KCNS	148·7	−48·62	123·07	−23·0
RbCNS	148·7	−54	118·297	−23·6

* Significant only to two figures.
† $\Delta H_f(M^+g)$ heat of formation of gaseous metal ion, data from ROSSINI *et al.*[8]
‡ $\Delta H_f(MXc)$ heat of formation of crystalline compound, data from ROSSINI *et al.*[8]

[9] K. B. YATSIMIRSKII, *Izv. Akad. Nauk SSSR, Otdel. khim. nauk* 411, 453 (1947); 398, (1948).
[10] A. F. KAPUSTINSKII, *Acta Physicochim. U.R.S.S.* **18**, 370 (1943).

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formal charges of the cation and anion, and r_1 and r_2 are the Goldschmidt radii of cation and anion (Å). The equation takes into account only the contributions to the lattice energy of Coulomb forces and repulsion forces between nearest neighbours (unlike ions). Also, where polyatomic ions with non-spherical symmetry are involved, the ions are assumed to have an "average radius" and equivalent central point charge.

TABLE 5.—VALUES OF $\Delta H_f(X^-g)$ OBTAINED FROM THE WORK OF YATSIMIRSKII
[Values in kcal/g ion (289°K)]

NO_2^-	ClO_3^-	ClO_4^-	NO_2^-	IO_3^-	CNS^-
−76·5	−54·3	−88·0	−29·2	−77	−8

YATSIMIRSKII's figures are based on heats of formation for positive ions taken from the compilation of BICHOWSKY and ROSSINI,[11] but some of these values are as much as 10 kcal in error, causing errors up to 5 kcal in the heats of formation of the negative ions. The figures quoted here have been derived by PRITCHARD,[12] who has corrected the original figures by an amount (3·5 kcal) representing the mean difference between YATSIMIRSKII's and the present values for the halogens.

Values of $\Delta H_f(X^-g)$ obtained from YATSIMIRSKII's work are given in Table 5 for comparison with the figures in Table 4. It can be seen that the agreement between the values of YATSIMIRSKII and those derived in the present work is really satisfactory only in the case of NO_3^-.

LATTICE ENERGIES OF OTHER COMPOUNDS

In the previous section equation (2) was used to derive values of $\Delta H_f(X^-g)$ from data for crystals where the lattice energy had been derived using lyotropic numbers. These $\Delta H_f(X^-g)$ values may in turn be employed in equation (2) to derive lattice energies for other compounds. Some results obtained in this manner are quoted in Table 6.

It has been demonstrated that the lattice energies of the alkali halides exhibit a striking regularity.[3] Within the limits of experimental error, the lattice energies of sodium halides are equal in magnitude to the mean of the lattice energies of the corresponding lithium and potassium halides, similarly the lattice energies of the rubidium halides approximate to the mean of the lattice energies of the corresponding potassium and caesium salts. This "mean rule" is also found to apply in the case of alkali metal azides if values of the lattice energies adopted by GRAY and WADDINGTON[7] are taken. If it is assumed that the "mean rule" is generally applicable within the limits of experimental error to alkali metal salts of the types listed in Table 3, estimates can be made of the lattice energies of some of those salts for which values of S are not available. Thus, for example, from the values of the lattice energies of $KClO_3$ and $RbClO_3$ listed in Table 3, a value of $U = 159{\cdot}4$ kcal mole^{-1} may be estimated for $CsClO_3$. Moreover, for such a compound an estimate of the heat of solution S may be made, by utilizing the value of the lattice energy derived by the "mean rule" and the corresponding value of H obtained from Fig. 1.

[11] F. R. BICHOWSKY and F. D. ROSSINI, *The Thermochemistry of the Chemical Substances*. Reinhold Publishing Corporation, New York (1936).
[12] H. O. PRITCHARD, *Chem. Rev.* **52**, 529 (1953).

TABLE 6.—LATTICE ENERGIES OF FURTHER COMPOUNDS
[Data are enthalpies in kcal mole^{-1} (298°K)]

Compound	ΔH_f(MXc)	ΔH_f(M^{n+}g)	ΔH_f(X^-g)	U
NH_4NO_3(IV)	−87·27	150	−79·1	158·2
$AgNO_3$(II)	−29·43	245·274	−79.1	195·6
$TlNO_3$(III)	−58·01	185·64	−79·1	164·6
$Ca(NO_3)_2$	−224·00	463·64	−79·1	529·4
$Sr(NO_3)_2$	−233·25	427·75	−79·1	502·8
$Ba(NO_3)_2$	−237·06	395·705	−79·1	474·6
$Pb(NO_3)_2$	−107·35	566·89	−79·1	516·0
$AgClO_3$	−5·73	245·274	−47·1	203·9
$Ba(ClO_3)_2$	−181·7	395·705	−47·1	483·2
NH_4ClO_4(II)	−69·42	150	−62·4	157·0
$AgClO_4$	−7·75	245·274	−62·4	190·6
$Ba(ClO_4)_2$	−192·8	395·705	−62·4	463·7
$LiNO_2$	−96·6	162·860	−45·9	213·6
NH_4NO_2	−63·1	150	−45·9	167·2
$AgNO_2$	−10·605	245·274	−45·9	210·0
$Ca(NO_2)_2$	−178·3	463·64	−45·9	550·1
$Sr(NO_2)_2$(II)	−179·3	427·75	−45·9	515·3
$Ba(NO_2)_2$	−174·0	395·705	−45·9	477·9
$Pb(CNS)_2$	27·5	566·89	−23·6	492·2

HYDRATION HEATS OF ANIONS

Although only ion hydration heat sums H can be determined experimentally, it is possible to split up the hydration heats of pairs of ions into the separate contributions of cation W_{M^+} and anion W_{X^-}

$$H = -(W_{M^+} + W_{X^-}). \tag{4}$$

The problem of dividing up these sums has been studied by LATIMER *et al.*[1] on the basis of the equation of BORN.[13] VERWEY[14] and RICE[15] have also made studies of the problem. The different investigators have produced almost identical sets of heats of hydration of certain ions, including data for the alkali metal cations. The hydration heats of the individual anions considered in the present paper may therefore be derived from values of H, obtained by interpolation in Fig. 1, together with the hydration heats of alkali metal cations due to LATIMER *et al.* Results are quoted in Table 7.

TABLE 7.—HEATS OF HYDRATION OF ANIONS, W_{X^-}
[Values in kcal mole^{-1} (298°K)]

NO_3^-	ClO_3^-	ClO_4^-	NO_2^-	IO_3^-	CNS^-	BrO_3^-
78·2	84·4	76·9	87·4	113·3	67·2	91·6

[13] M. BORN, *Z. Phys.* **1**, 45 (1920).
[14] E. J. W. VERWEY, *Rec. trav. chim.* **61**, 127 (1942).
[15] O. K. RICE, *Electronic Structure and Chemical Binding*. McGraw-Hill, New York (1940).

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ELECTRON AFFINITIES

It is possible to derive the electron affinities E of some molecules and radicals from the equation

$$E = \Delta H_f(\mathrm{Xg}) - \Delta H_f(\mathrm{X^-g}) \qquad (5)$$

using the $\Delta H_f(\mathrm{X^-g})$ data of Table 4. For cases where heats of formation of the species, $\Delta H_f(\mathrm{Xg})$, are known, results are quoted in Table 8.

TABLE 8.—ELECTRON AFFINITIES
[Data in kcal mole^{-1} (298°K)]

Molecule or radical	$\Delta H_f(\mathrm{Xg})$	$\Delta H_f(\mathrm{X^-g})$	E
NO_2	8·1	−45·9	54·0
NO_3	13	−79·1	92·1
ClO_3	37·0	−47·1	84·1
ClO_4	(46)*	−62·4	108·4

* Assuming D(Cl—O) = 55 kcal mole^{-1}.

DISCUSSION

The relative lyotropic effects of ions are due to their different electrostatic field strengths.[5] This is illustrated, for example, by the relationship between lyotropic numbers and heats of hydration of ions; it is also supported in the case of alkali metal cations by ionization potentials I, which are in approximately linear relationship with the lyotropic numbers—Fig. 2.

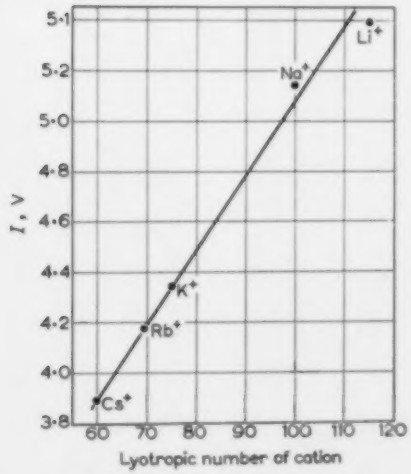

FIG. 2.—Ionization potentials of alkali metals plotted against lyotropic numbers.

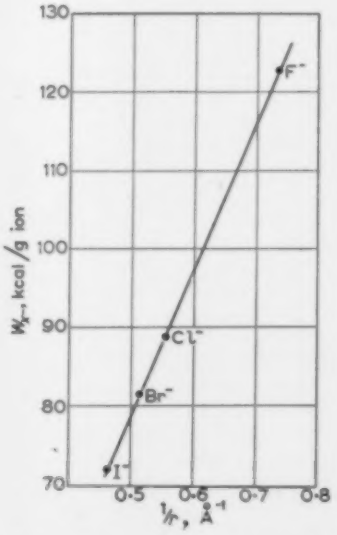

FIG. 3.—Relationship between hydration heats of halide ions and Pauling crystal radii.

In considerations of electrostatic attractions involving spherically symmetrical monatomic ions, it is generally a satisfactory approximation to regard the ions as having their formal charge as a central point charge and to take the potential energy of their electric fields as being inversely proportional to their crystal radii. Thus for halide ions a linear relationship between the reciprocal of the ionic (crystal) radius and ion hydration heat is obtained—Fig. 3. For unsymmetrical ions, such as ClO_3^-, BrO_3^- and IO_3^- which have a pyramidal structure (Fig. 4), such a simple regularity does

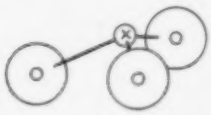

FIG. 4.—The structure of an oxyhalide ion XO_3^-.

not apply. Thus the data of Tables 3 and 7, based on lyotropic numbers, show that for the oxyhalide ions XO_3^- the potential energies are in the order iodate > bromate > chlorate although the sizes of the ions also lie in that order. This conclusion can be correlated with the fact that in sodium chlorate and sodium bromate, which have similar crystal structures,[16] the Na–O distance is smaller in the bromate (2·38 Å) than in the chlorate (2·48 Å).

[16] R. W. G. WYCKOFF, *Crystal Structures*. Interscience, New York (1951).

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J. Inorg. & Nucl. Chem., 1958, Vol. 6, pp. 303 to 307. Pergamon Press Ltd., London

THE NUCLEAR MAGNETIC RESONANCE OF FLUORINE IN FLUOROSILANES

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(*Received* 22 *August* 1957)

Abstract—The ^{19}F nuclear magnetic resonance in methyl- and ethyl-fluorosilanes was measured relative to diethyldifluorosilane, both for the pure substances and for solutions at varying concentration in carbon tetrachloride. The "chemical shift" of fluorine (especially at infinite dilution in carbon tetrachloride) is considered in relation to the structure of the compounds and the bonding properties of silicon. The ^1H nuclear magnetic resonances of the methyl- and ethyl-chloro- and fluoro-silanes (relative to water) also were measured, and no separation of the proton resonance in $—CH_3$ and $—CH_2—$ groups was found.

THE shift in the resonance frequency (at constant magnetic field) of the ^{19}F nucleus in going from silicon tetrafluoride to the various organo-substituted fluorosilanes should shed some light on the nature of the bonding in such organosilicon substances, and hence we undertook a study of this "chemical shift" in relation to structure[1]. This paper reports the results of this initial study, and considers the various factors that might be responsible for these results. In addition, the resonance of the ^1H nuclei in the same organofluorosilanes (and in the corresponding organochlorosilanes) has been investigated and is discussed in relation to the same structural bonding factors.

The principles of nuclear magnetic resonance are covered in several works which have now become standard references,[2] and need not be repeated here. We are concerned only with the so-called "chemical shift" in the resonance frequency of a nuclear species in a constant external magnetic field, such shift (from the frequency of the same resonating species in some substance taken as standard) reflecting the electronic bonding environment of the species. Due to the influence of neighbouring molecules of the same sort and to the influence of the bulk magnetic susceptibility of the medium, it often is prudent to measure the "chemical shift" in solutions of differing concentration in a suitable solvent[3] and then to extrapolate the results to infinite dilution.

EXPERIMENTAL

The substances CH_3SiF_3, $(CH_3)_2SiF_2$, $(CH_3)_3SiF$, $C_2H_5SiF_3$, $(C_2H_5)_2SiF_2$, and $(C_2H_5)_3SiF$ were prepared in a vacuum system by the reaction of the corresponding methyl- and ethyl-chlorosilanes with anhydrous zinc fluoride,[4] and their boiling points were all in good agreement with those previously reported.[4] All but

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[1] E. SCHNELL and E. G. ROCHOW, *J. Amer. chem. Soc.* **78**, 4178 (1956).

[2] E. M. PURCELL, *Science* **107**, 433 (1948); E. M. PURCELL, H. C. TORREY and R. V. POUND, *Phys. Rev.* **69**, 37 (1946); E. R. ANDREW, *Nuclear Magnetic Resonance*. Cambridge Univ. Press, London (1955).

[3a] A. A. BOTHNER-BY and R. E. GLICK, *J. Amer. chem. Soc.* **78**, 1071 (1956); [b] A. L. ALLRED Thesis, Harvard University (1956); [c] A. L. ALLRED and E. G. ROCHOW, *J. inorg. nucl. Chem.* **5**, 264(1957).

[4] H. J. EMELEUS and C. J. WILKINS, *J. chem. Soc.* 454 (1944); A. E. NEWKIRK, *J. Amer. chem. Soc.* **68**, 2736 (1946).

triethylfluorosilane were also prepared by the reaction of boron trifluoride etherate on the corresponding silanols or siloxanes,[5] and these preparations (after purification by fractional distillation) had the same boiling points and exhibited fluorine resonances at exactly the same frequency as the samples prepared by the zinc fluoride method.

The substances which were liquid at room temperature were sealed in 5 mm sample tubes containing a 1 mm sealed capillary of reference substance.[3a] Diethyldifluorosilane was used as reference substance in most of the measurements because it could readily be purified and because it has a convenient boiling point (60·9°); this in turn was compared with trifluoracetic acid, the standard used by GUTOWSKY

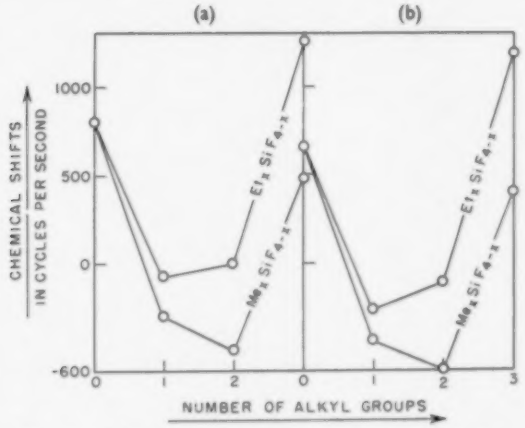

FIG. 1.—Chemical shifts of ^{19}F resonance versus number of alkyl groups in R_xSiF_{4-x}; (a) in the pure compounds and (b) in infinitely dilute solutions in carbon tetrachloride.

and HOFFMAN.[6] The substances CH_3SiF_3 and $C_2H_5SiF_3$ were too volatile to be sealed in sample tubes of this type; they could best be handled by admitting them from the vacuum system to a separable bulb of 100 ml capacity to which was sealed a closed condensing tube 5 mm in diameter and 100 mm long. The gaseous sample was condensed in the 5 mm tube, which also served as sample tube for the measurements. The substance remained in the liquid phase long enough for a measurement easily to be made, and the same sample could be condensed and used over in this way without problems of storage under pressure. Silicon tetrafluoride could not be handled even in this device, however, because it sublimes and forms no liquid save at impossibly high pressures. Its resonance therefore was measured in solution in carbon tetrachloride and in *n*-hexane at varying concentrations, and the value for the pure substance was obtained by extrapolation.*

All measurements were made on a Varian Type V-4300B high-resolution nuclear magnetic resonance spectrometer in conjunction with a 12 in. magnet. The sample tubes were spun by an air turbine to average local inhomogeneities. Proton resonances were obtained relative to water on the same equpiment, of course at a different level

* We measured SiF_4 and CF_2COOH vs. Et_2SiF_2, but the resulting total shift of SiF_4 vs. CF_2COOH (3479 cycles) agrees well with that found by GUTOWSKY and HOFFMAN[3] by direct comparison.

[5] H. GROSSE-RUYKEN, *Z. angew. Chem.* **66**, 754 (1954).
[6] H. S. GUTOWSKY and C. J. HOFFMAN, *Phys. Rev.* **80**, 110 (1950); *J. chem. Phys.* **19**, 1259 (1951); *Ibid.* **20**, 200 (1952).

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of magnetic field strength. The shift in frequency between sample and standard was measured with a precision oscillator with a probable error of ±2 per cent.[3] The results for both fluorine and hydrogen resonance are given in Table 1.

TABLE 1.—CHEMICAL SHIFTS OF THE FLUORINE AND PROTON RESONANCES IN FLUOROSILANES, SILICON TETRAFLUORIDE AND CHLOROSILANES

Compound	F resonance compared with Et_2SiF_2 (c/s)			Proton resonance compared with water (c/s)		
	pure cpd.	inf. dil.	shift (p.p.m.*)	pure cpd.	inf. dil.	shift (p.p.m.*)
CF_3COOH	−2665	not meas.	−66·7	—	—	—
Me_2SiF	+505	+404	+10·1	+205	+190	+4·75
Me_2SiF_2	−490	−608	−15·2	+203	+164	+4·10
$MeSiF_3$	−298	−440	−11·0	+201	+145	+3·63
SiF_4	+814	+665	+16·6	—	—	—
Et_2SiF	+1260	+1181	+29·5	+169	+148	+3·70
Et_2SiF_2	0	−110	−2·75	+167	+155	+3·88
$EtSiF_3$	−82·7	−265	−6·63	+167	+150	+3·75
$PhSiF_3$	−88	−183	−4·57	−81	−114	−2·85
$ViSi_3$	−55	−220	−5·50	−69	−52	−1·30
Me_4Si				+210	+195	+4·88
Me_3SiCl				+248	+149	+3·73
Me_2SiCl_2				+165	+158	+3·95
$MeSiCl_3$				+149	+140	+3·50
Et_3SiCl				+158	+157	+3·93
Et_2SiCl_2				+170	+139	+3·48
$EtSiCl_3$				+145	+142	+3·55
$ViSiCl_3$				−56	−63	−1·58

* Parts per million, obtained by dividing the values for chemical shift at infinite dilution in the preceding column (in cycles per second) by the resonance frequency (40·01 Mc/s).

DISCUSSION

Fig. 1 (a and b) shows the trend of the chemical shift of fluorine in cycles per second for the pure liquid compounds and for solutions at infinite dilution in carbon tetrachloride. Since no change in the sequence of the shifts for the infinitely dilute solutions is observed, it seems reasonable to use the values for the pure compounds. If so, the value obtained for silicon tetrafluoride can also be compared with the value reported by GUTOWSKY and HOFFMAN,[6] which is not distinctly different.

A preliminary explanation for the fluorine chemical shifts of the compounds measured has already been given.[1] It seems reasonable to attribute changes in the magnitude of the chemical shielding of the fluorine atoms to two main effects, the first of which is a π-bonding effect.[7] Let us assume that the silicon atom uses its *d* orbitals for Si—F $d\pi$—$p\pi$ bonding to an amount which does not vary considerably with the number of fluorine atoms surrounding the silicon. This would mean that if only one fluorine is bonded to the silicon this fluorine atom would be less shielded

[7] F. G. A. STONE and D. SEYFERTH, *J. inorg. nucl. Chem.* **1**, 112 (1955).

than one of the fluorine atoms in SiF_4. The chemical shifts caused by this effect will then vary in a manner like that shown in Fig. 2a.

The second effect is a rather conventional inductive effect which will increase with the number of alkyl groups and will increase from methyl to ethyl. The electron

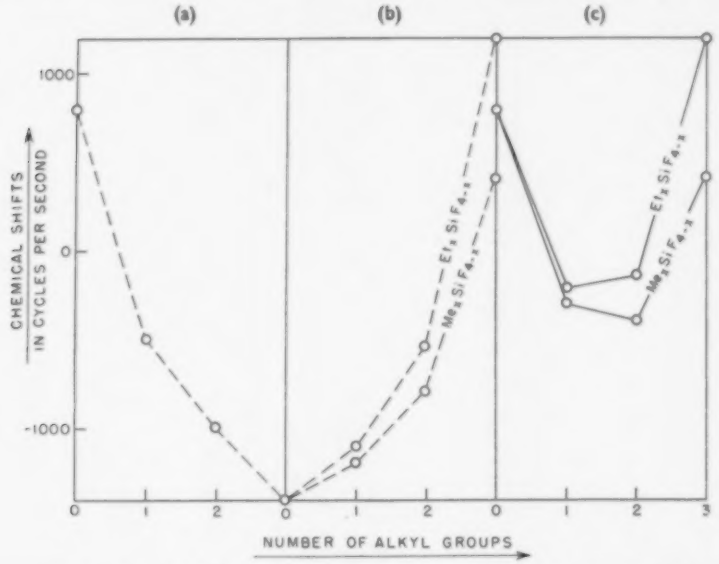

FIG. 2.—Chemical shifts of ^{19}F resonance versus number of alkyl groups in R_xSiF_{4-x}: (a) Expected relative ^{19}F shielding due to $d\pi$–$p\pi$ bonding, (b) Expected relative inductive effect of methyl and ethyl groups, and (c) Combination of the effects in (a) and (b).

release by the alkyl groups will increase in magnitude about three times when changing from monoalkyl to trialkyl silanes. As there are three fluorine atoms in the monoalkyl trifluorosilane and one in the trialkyl fluorosilane, the magnitude of the effect on one of the fluorine atoms in these compounds will increase from $\frac{1}{3}$ to 3, or in the ratio 1 to 9 (Fig. 2b). Adding these values to the values caused by the first effect will show the kind of variation of the chemical shifts given in Fig. 2c. Aside from these two main effects there will almost certainly be minor ones, but the two already considered are seen to account for the main features.

The proton resonances (relative to water) of the fluorosilanes and chlorosilanes are given in the last two columns of Table 1. It is evident that (a) the proton shifts are small in comparison with those of fluorine,[8] and (b) the changes upon dilution vary greatly from one compound to the next. In view of such fluctuations it seems best to consider only the values at infinite dilution, which are plotted in Fig. 3. The most marked changes are seen to occur in the methylfluorosilane series, where contribution of electrons by the fluorine to the silicon in the manner just considered makes the silicon more electron-rich. As has clearly been shown by ALLRED,[3b,c,9] the more positive the atom or group attached to a methyl group, the greater will be the proton shift of the methyl group relative to water. As fluorine atoms are replaced by methyl groups in the present series, the silicon becomes more electropositive and

[8] A. SAIKA and C. P. SLICHTER, *J. chem. Phys.* **22**, 26 (1954).
[9] A. L. ALLRED and E. G. ROCHOW, *J. Amer. chem. Soc.* **79**, 5361 (1957).

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the shift increases. A similar change in the effective electronegativity of silicon due to contribution of electrons to its *d* orbitals has been noted in silicon–oxygen compounds[10]. The poorer donor ability of chlorine relative to fluorine or oxygen would be expected to lead to the more minor variations in the lower curves of Fig. 3.

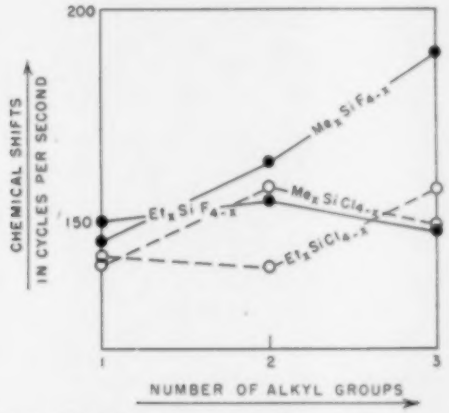

FIG. 3.—Chemical shift of ^{1}H resonance in methyl- and ethyl-fluorosilanes and chlorosilanes.

With normal resolution of the instrument no separation of the resonance lines of CH_3— or —CH_2— groups could be found, either in the fluorosilanes or in chlorosilanes. Similar observations have been made by ALLRED[11] in this laboratory, and according to PIPER and WILKINSON[12] the methyl and methylene resonances might be expected to coalesce when the "electronegativity" of the atom bound to the ethyl group is below about 1·7 (and probably below about 1·9.[3b,c]) Vinyltrifluorosilane (the preparation and properties of which will be reported elsewhere) also shows no separation of CH_2= and —CH= resonances.

Since the vinyl group (Vi in the table) and the phenyl group have inductive effects very different from those of the two lowest alkyl groups, and since both vinyl and phenyl groups may also participate in $d\pi$–$p\pi$ bonding to silicon, the proton resonances are far removed from those of the methyl and ethyl groups. They indicate even less shielding for hydrogen than in water (negative shift), and so indicate extreme withdrawal of electrons from the H—C bond by the π-active group. The same $d\pi$–$p\pi$ bonding activity by the phenyl and vinyl groups should make increasing numbers of fluorine atoms less effective (since the maximum amount of $d\pi$–$p\pi$ bonding by silicon seems limited), and the vinyl- and phenyl-trifluorosilanes are indeed seen to show less fluorine shift than the methyl- and ethyl-trifluorosilanes (first two columns, Table 1). It will be interesting to extend the study to other olefinic and aromatic fluorosilanes.

Acknowledgements—We wish to thank the U.S. State Department for a National Academy of Sciences fellowship (E. S.), and the Esso Education Foundation for assistance in the purchase of equipment.

[10] A. L. ALLRED, E. G. ROCHOW and F. G. A. STONE, *J. inorg. nucl. Chem.* **2**, 416 (1956).
[11] A. L. ALLRED, Private communication.
[12] B. P. DAILEY and J. N. SCHOOLERY, *J. Amer. chem. Soc.* **77**, 3977 (1955); T. S. PIPER and G. WILKINSON *J. inorg. nucl. Chem.* **3**, 122 (1956).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 308 to 313. Pergamon Press Ltd., London

PHOSPHATES AND POLYPHOSPHATES OF THE RARE EARTH ELEMENTS—II

PYROPHOSPHATO AND TRIPHOSPHATO COMPLEXES OF NEODYMIUM AND YTTRIUM

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(*Received* 30 *October* 1957; *in revised form* 1 *January* 1958)

Abstract—The hydrogen ion displacement method has been employed to verify formation of the normal phosphate, pyrophosphate and triphosphate of yttrium when precipitation of these substances is effected by reaction of aqueous solutions adjusted to pH of 4·5. Titration of yttrium and neodymium salts with standard solutions of pyro- and triphosphates indicates (a) formation of the normal pyro- and triphosphates in the more acid solutions and (b) in the case of triphosphate, the formation of a soluble anionic species in which the ratio of rare earth metal ion to triphosphate is 1:2. Solution of rare earth pyrophosphates in excess of pyrophosphate can also be effected. Elution of these rare earths from a typical cation exchange agent (Amberlite IR-120) with triphosphate at pH of 8·5 affords additional evidence for formation of the bis-triphosphato rare earth complex. Larger ratios of pyrophosphate to rare earth are needed to effect elution with pyrophosphate. The absorption spectrum of a solution of the bis-triphosphato neodymium complex differs only slightly from that of an aqueous neodymium chloride solution.

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WE were impressed early in our studies[1] with the fact that the pyro- and triphosphates of the rare earth elements dissolve in an excess of either tetrasodium pyro- or pentasodium triphosphate, respectively. Solutions of such pyrophosphato and triphosphato complexes of the rare earths are obtained only over rather definite pH ranges. Large excesses of pyrophosphate are required to dissolve the rare earth pyrophosphates in contrast to the relatively small amounts of triphosphate needed to dissolve the respective rare earth triphosphates. The possible usefulness of these preliminary observations to effect separation of the rare earth elements from each other and of the rare earth elements from accompanying elemental species made it desirable to study these findings in more detail. The second paper of this series of articles is therefore devoted primarily (a) to a study of the pyrophosphato and triphosphato complexes of neodymium and of yttrium, and (b) to a preliminary investigation of the usefulness of pyrophosphate and triphosphate in the form of their sodium salts as alkaline "sequestering" eluants for removal of rare earths from a typical cationic exchange-resin.

The possible use of triphosphate as a complexing agent for heavy metal ions was suggested by a number of very interesting qualitative observations first recorded by FRANKENTHAL *et al.*[2] who noted that solutions of a large number of metallic salts including some of the rare earths (Y, La, Ce, Pr, Nd and Sm) and other rare

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[1] A. G. BUYERS, E. GIESBRECHT and L. F. AUDRIETH, *J. inorg. nucl. Chem.* **4**, 153 (1957).
[2] L. FRANKENTHAL, J. S. ROBERTS and C. NEUBERG, *Exp. med. Surgery* **1**, 395 (1943).

metals, such as thorium, uranium (as UO_2^{++}), indium and thallium "are not precipitated by $Na_5P_3O_{10}$, or the precipitates produced are dissolved completely in excess of triphosphate". These same investigators further emphasize the remarkable complexing power of triphosphate by calling attention to the many "atypical reactions occurring in the presence of $Na_5P_3O_{10}$" including "the existence in solution of CaF_2, $BaSO_4$, CaC_2O_4, of carbonates and orthophosphates of nearly all of the elements, and of some normally insoluble sulphides". The strong complexing abilities of the polyphosphates have been discussed by VAN WAZER and CAMPANELLA[3] who have proposed that chelation involving adjacent PO_4 tetrahedra in the polyphosphate chains might very well account for the behaviour of these chain-molecule ions as co-ordinating groups. Chelate structures for polyphosphate complexes have also been proposed by BOBTELSKY and KERTES,[4] by MARTELL and SCHWARZENBACH[5] and by WATTERS *et al.*[6]

EXPERIMENTAL

The phosphates and polyphosphates of yttrium

The hydrogen ion displacement method described in the first paper of this series[1] was used to show that the normal yttrium phosphate, pyrophosphate and triphosphate salts are formed when yttrium solutions adjusted to a pH of 4·5 are allowed to react with the respective phosphate or polyphosphate solutions, also adjusted to a pH of 4·5. Excesses of the phosphate or polyphosphate varying from 10 to 100 per cent were added dropwise with constant stirring to the rare earth solutions. The displaced hydrogen ion was then determined, usually within one-half hour after the addition of phosphate solution, by back-titration to pH of 4·5 with standard base. Typical experimental data are summarized on Table 1.

TABLE 1.—FORMATION OF PHOSPHATES AND POLYPHOSPHATES OF YTTRIUM

Weight oxide (g)	Y^{3+} moles $\times 10^{-3}$	Phosphate added	Standard base 0·1 N (ml)	H^+ displaced (moles $\times 10^{-3}$)	Ratio H^+/Y^{3+}	Average atomic weight	
						H^+ displacement method	Oxalate–permanganate method
0·1127	0·998	$H_2PO_4^-$	19·63	1·96	1·97	90·7	89·5
0·1127	0·998	$H_2PO_4^-$	19·65	1·97	1·97	90·7	89·4
0·1127	0·998	$H_2P_2O_7^-$	14·22	1·42	1·43	—	—
0·1127	0·998	$H_2P_2O_7^{--}$	14·86	1·49	1·49	—	—
0·1127	0·998	$H_2P_3O_{10}^{---}$	11·81	1·18	1·18	—	—
0·1127	0·998	$H_2P_3O_{10}^{---}$	11·92	1·19	1·19	—	—

* 100% excess sodium dihydrogen pyrophosphate solution.

As pointed out in the first paper of this series, the dihydrogen phosphate–rare earth titration procedure can be employed to determine the average atomic weight of individual rare earths or of rare earth mixtures by application of the relationship:

$$\frac{R_2O_3}{4\,H^+} = \frac{\text{wt. of rare earth oxide}}{(\text{normality of NaOH})(\text{ml})(0{\cdot}001008)}.$$

[3] J. R. VAN WAZER and D. A. CAMPANELLA, *J. Amer. chem. Soc.* **72**, 655 (1950).
[4] M. BOBTELSKY and S. KERTES, *J. appl. Chem.* **4**, 419 (1954); **5**, 125, 675 (1955).
[5] A. E. MARTELL and G. SCHWARZENBACH, *Helv. chim. Acta* **39**, 653 (1953).
[6] J. I. WATTERS, S. M. LAMBERT and E. D. LOUGHRAN, *J. Amer. chem. Soc.* **79**, 3651 (1957).

The atomic weight of the yttrium sample used in this study was found to be somewhat higher than that determined by use of the standard oxalate–permanganate procedure.

The hydrogen ion displacement method was also employed to verify the formation of yttrium pyrophosphate and of yttrium triphosphate. Solutions of known yttrium content were adjusted to a pH of 4·5 and then treated with pyrophosphate and triphosphate solutions, also adjusted to the same pH. The liberated hydrogen ion was determined by back titration with standard base. Theoretical hydrogen ion to yttrium ion ratios of 1·5 and 1·2, respectively, would be required on the basis of the following reactions:

$$4Y^{3+} + 3H_2P_2O_7^{--} \rightarrow Y_4(P_2O_7)_3 + 6H^+ \quad (2)$$

$$5Y^{3+} + 3H_2P_3O_{10}^{--} \rightarrow Y_5(P_3O_{10})_3 + 6H^+ \quad (3)$$

Experimentally determined values are somewhat lower, but are sufficiently close to the theoretical figures to demonstrate that the normal pyro- and triphosphates of

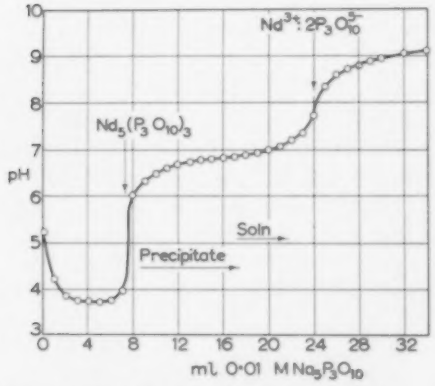


FIG. 1.—Titration of a 0·01 M neodymium chloride solution (12 ml) with 0·01 M sodium triphosphate solution.

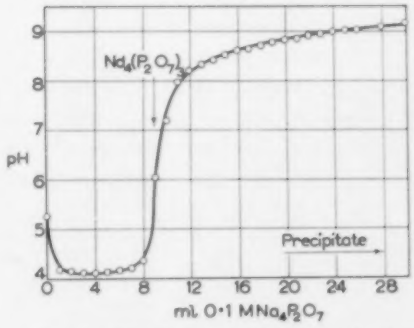


FIG. 2.—Titration of a 0·1 M neodymium chloride solution (12 ml) with 0·1 M sodium pyrophosphate solution.

yttrium are formed. It is apparent, however, that incomplete precipitation of yttrium pyrophosphate takes place if stoicheiometric quantities of the reactants are employed. If an excess of pyrophosphate agent is added, however, a hydrogen ion to yttrium ion ratio is obtained which suggests that essentially complete precipitation has occurred.

pH *changes during titrations of neodymium* (III) *and yttrium* (III) *with polyphosphates*

The curves depicting changes in pH when solutions of yttrium or neodymium salts are titrated with standard solutions of sodium pyro- and triphosphates (see Figs. 1 and 2) indicate clearly (a) the formation of the normal pyro- and triphosphates in the more acid solutions and (b) in the case of the triphosphates, the formation of complex anionic species in which the ratio metal ion to triphosphate is 1 : 2. Reverse titrations entailing addition of rare earth solutions to polyphosphate solutions (see Figs. 3 and 4) further show that the pH range over which soluble complexes

exist is much greater for the triphosphate than for the pyrophosphate. The solubilization of yttrium and neodymium triphosphates is accomplished by use of relatively smaller amounts of sodium triphosphate solution and begins at a pH between 6·0–7·0. Precipitates containing the respective polyphosphates contaminated with the hydroxides are obtained when excess base is added to such solutions.

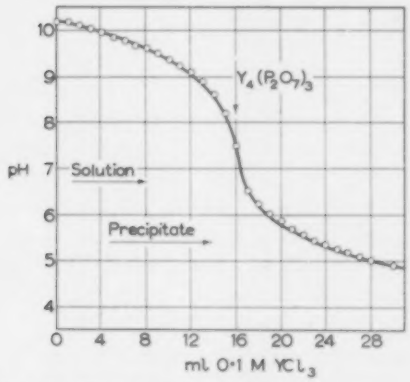


FIG. 3.—Titration of a 0·1 M sodium pyrophosphate solution (12 ml) with 0·1 M yttrium chloride solution.

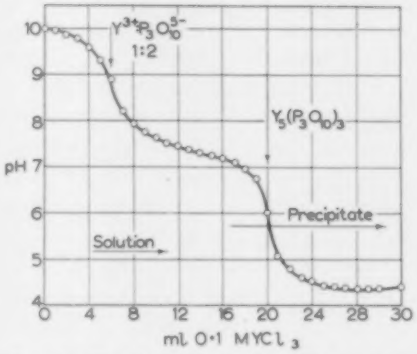


FIG. 4.—Titration of a 0·1 M sodium triphosphate solution (12 ml) with 0·1 M yttrium chloride solution.

An anomalous drop in pH was found to occur at the beginning of the titration of both rare earth salts by polyphosphate solutions (see Figs. 1 and 2). It is probable that direct addition of the strongly alkaline polyphosphate solutions causes partial formation of basic salts. Even so, these products are dissolved completely when excess polyphosphate solution is added. Other investigators have noticed a similar change in titrations of this sort.[4,7]

Removal of neodymium and yttrium from cation exchange resins

The yttrium and neodymium forms of the ion exchange resin were prepared from Amberlite IR-120 (hydrogen form, 40–60 mesh) by slurrying with excesses of yttrium or neodymium chloride solutions. The residual solutions were decanted from the resins after 24 hr; the resins were washed several times with water and air-dried for 24 hr. Twelve-gramme samples of the dried rare earth resins, containing 0·0799 g yttrium or 0·132 g neodymium per gramme of resin, respectively, were used in all elution experiments. The appropriate resin was packed in a column 40 × 0·9 cm and washed with a very dilute solution of sodium hydroxide. The solution of sodium pyro- or triphosphate (0·05 M), whose pH had been adjusted to 8·5, was next passed through the column at a rate of about 60 ml/hr. One hundred ml fractions were collected periodically and analysed for their neodymium (yttrium) contents.

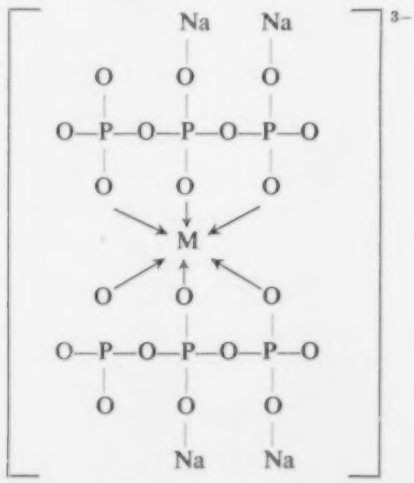
In a typical experiment entailing elution of a Nd–resin with 0·05 M $Na_5P_3O_{10}$ solution the first four 100 ml fractions of eluate were found to contain 0·3743 g Nd (0·0026 moles) each. This corresponds to a $Nd^{3+}:P_3O_{10}^{5-}$ ratio of 1 : 1·92. The fifth fraction contained the remainder of the rare earth, recovery from the resin amounting to 99·5 per cent. Similar observations characterized elution of an Y–resin

[7] L. B. ROGERS and C. A. REYNOLDS, *J. Amer. chem. Soc.* **71**, 2081 (1949).

with each of the first four 100 ml fractions of eluate containing 0·2209 ± 0·0002 g Y (0·00248 moles), corresponding to a $Y^{3+} : P_3O_{10}^{5-}$ mole ratio of 1 : 2·02. Here again the fifth 100 ml fraction of eluate contained the remainder of the Y^{3+} with total recovery of the rare earth from the resin amounting to 99·84 per cent.

Elution of a Nd–resin with pyrophosphate was found to be much less efficient. After a steady state had been achieved the ratio of $Nd^{3+} : P_2O_7^{4-}$ in the eluate was found to be 1 : 4. Relatively large amounts of pyrophosphate are required for complete elution of the rare earths from the resins.

Elution studies indicate the preferential formation of a bis-triphosphato rare earth complex under the indicated pH conditions. Although these results suggest formation of a triphosphato complex ion with the formula $M(P_3O_{10})_2^{7-}$ it seems highly improbable that such a highly charged anionic species actually exists. The true composition is more adequately expressed by the formula $[Na_xM(P_3O_{10})_2]^{(7-x)-}$ in which x is some value less than 7. Even sodium triphosphate in the alkaline range yields species in which the larger percentage of the sodium is complexed with the triphosphate anion, as indicated by transference measurements using radioactive sodium ion.[8] The structure of an anionic complex with the formula $[Na_4M(P_3O_{10})_2]^{3-}$, assuming formation of multiple chelate rings to conform with the hexacovalency of the rare earth ion may be represented as follows:



Attempts to isolate the neodymium and yttrium polyphosphato-compounds were not particularly successful. In a typical experiment, a large excess of 0·1 M sodium pyrophosphate solution was added to a 0·1 M neodymium chloride solution ($Nd^{3+} : P_2O_7^{4-} = 1 : 12$), to give a light pink solution, pH of 9·5. After standing for two weeks at room temperature, a precipitate began to form. After one more week, the precipitate was removed by filtration and washed successively with cold water, alcohol and ether. The product was dried in a desiccator and then at 110°C to constant weight. The light pink microcrystalline solid was subjected to analysis.

(*Anal.* Found: Na, 12·7; Nd, 29·42; P, 16·93. Calc. for $Na_4P_2O_7 \cdot 3NaNd(P_2O_7) \cdot 10H_2O$: Na, 10·95; Nd, 29·45; P, 16·86.)

[8] F. T. WALL and R. H. DOREMUS, *J. Amer. chem. Soc.* **76**, 868 (1954).

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Addition of sodium triphosphate solution to neodymium chloride or perchlorate solutions in quantities corresponding to a $Nd^{3+} : P_3O_{10}^{5-}$ ratio 1 : 2 yielded a viscous pink oil when treated with an equal volume of ethyl alcohol. The oil was decanted, washed many times with alcohol, and then with ether to bring about solidification. The product was triturated, washed again with alcohol and ether, and dried in the oven at 110°C to give a pink amorphous, hygroscopic solid. Solubilisation in water could be effected only very slowly. The Nd : P ratio was found by analysis to be 1 : 5·96 and the sodium content, 17·6 per cent (calc. for $Na_7Nd(P_3O_{10})_2$, 19·98 per cent). However, a paper chromatographic study of the aqueous solution of this product revealed presence of ortho-, pyro-, as well as higher polyphosphates. It is evident that some decomposition of the triphosphato complex had occurred during the drying treatment.

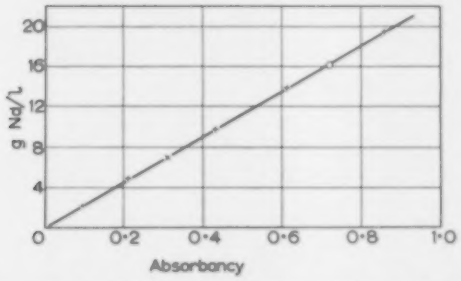

FIG. 5.—Absorbancy of a triphosphato neodymium solution at 5825 Å vs. concentration of neodymium (g/l.).

The absorption spectrum of polyphosphato-neodymium solutions

The absorption spectrum of solutions containing the triphosphato neodymium complex was found to differ only slightly from that of an aqueous neodymium chloride solution. A decrease in the absorbancy maximum and a slight shift in the lines was observed in such solutions. These differences were found to be independent of the amounts of added triphosphate. A plot of $[Nd^{+++}]$ vs. absorbency for the band at 5825 Å (Fig. 5) demonstrates that Beer's law holds for such solutions and that quantitative estimation of neodymium content can be effected spectrophotometrically. It should further be noted that the absorption spectrum of solutions of neodymium pyrophosphate in excess pyrophosphate reveals only a negligible difference from aqueous neodymium solutions.

Acknowledgements—It is a pleasure for one of us (E. G.) to acknowledge his indebtedness to the Rockefeller Foundation for a fellowship which made it possible for him to undertake the above investigation at the University of Illinois (1956–7). Our thanks are also extended to Professor G. THERALD MOELLER for helpful advice and suggestions and to personnel of the Victor Chemical Works Research Laboratories at Chicago Heights, Illinois, for their assistance.

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 314 to 318. Pergamon Press Ltd., London

SPECTROPHOTOMETRIC AND ELECTRICAL CONDUCTANCE STUDIES ON CHELATE FORMATION OF URANYL ION WITH AMMONIUM AURINTRICARBOXYLATE

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(*Received* 13 *October* 1957; *in revised form* 6 *December* 1957)

Abstract—The formation of a coloured chelate between uranyl ion and ammonium aurintricarboxylate with λ_{max} at 540 mμ, has been reported. The chelate has a composition of 1 : 1. The formation constant at 25°C is 5·9 ± 0·5 × 10^4, and the free energy of formation −6·51 ± 0·05 kcal at the same temperature.

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A CONSIDERABLE amount of work has been done on the analytical applications involving colour formation of metal ions with ammonium aurintricarboxylate,[1,2] but not much information is available on the study of metal chelates formed in these systems. We have undertaken a detailed study of metal chelates with ammonium aurintricarboxylate, and have in this connexion already studied the coloured chelates of bivalent copper[3] and trivalent iron.[4] In this paper we have described our results on the system uranyl sulphate–ammonium aurintricarboxylate, studied by spectrophotometric and electrical conductance measurements. An attempt has been made to throw light on the composition, structure and stability of the metal chelate formed, and the free energy of formation of the chelate has been calculated.

It may be mentioned that SMITH *et al.*[5] laid emphasis on the quality of the ammonium aurintricarboxylate (Aluminon Reagent) sample for colorimetric measurements. They determined suitable conditions necessary for the preparation of the reagent, and recommended that the addition of alkali must be avoided in order that a stable colour may be obtained. From electrical conductance studies,[6] we have found that the reagent behaves as a colloidal electrolyte and have observed that it is only in extremely dilute solutions that the compound shows the characteristics of a true solution. We have, hence, emphasized the use of very dilute solutions for the study by physicochemical methods,[7] of the composition of metal chelates involving Aluminon.

EXPERIMENTAL

Materials

BDH "Reagent" grade ammonium aurintricarboxylate was used and it was ascertained from the manufacturers[8] that the reagent was one prepared by the method of SMITH *et al.* The uranyl sulphate used was of BDH "Analar" grade. Solutions were always freshly prepared to minimize the possibility

* Present address: Coates Chemical Laboratory, Louisiana State University, Baton Rouge 3, La., U.S.A.

[1] W. C. JOHNSON, *Organic Reagents for Metals*. Chemical Publishing Co., New York (1955)
[2] A. K. MUKHERJI and A. K. DEY, *Z. analyt. Chem.* **152**, 424 (1956).
[3] A. K. MUKHERJI and A. K. DEY, *Anal. chim. Acta* **18**, 324 (1958).
[4] A. K. MUKHERJI and A. K. DEY, *Proc. natl. Acad. Sci. India* A **26**, 138 (1957).
[5] W. H. SMITH, E. E. SAGER and I. J. SIEWERS, *Analyt. Chem.* **21**, 1334 (1949).
[6] A. K. MUKHERJI and A. K. DEY, *J. Colloid Sci.* To be published.
[7] A. K. MUKHERJI and A. K. DEY, *Proc. Ind. sci. Cong.* **45** (3), 9 (1958).
[8] BRITISH DRUG HOUSES LTD., POOLE, Private communication.

of hydrolysis of the metal salt. Double distilled water, free from carbon dioxide, was used for making the solutions. Precautions were taken to exclude carbon dioxide, in view of the strong tendency towards complex formation between uranyl and carbonate ions.

Experimental procedure

A Unicam SP 500 Spectrophotometer was employed for the measurement of optical density, using the 10 mm glass cells supplied with the instrument. The experiments were carried out in an air-conditioned room maintaining 25°C. The individual solutions and the mixtures were kept in a Townson and Mercer thermostatic bath maintaining 25 ± 0·01°C, and the mixtures were allowed to stand in the thermostat for 15 min to attain equilibrium.

For the measurement of electrical conductance, a Leeds and Northrup Kohlrausch slidewire was employed, with an audiofrequency oscillator. The measuring cell was of the dip type, having a cell constant of 0·132. The solutions and the mixtures were kept in another thermostatic bath at 32 ± 0·01°C, before and during measurements.

pH measurements were made with a Leeds and Northrup pH meter, operated on 220 V/50 cycles single phase a.c. mains, with a glass-calomel electrode system, supplied with the instrument.

RESULTS

Nature of complexes formed

The method described by VOSBURGH and COOPER[9] was followed. Mixtures containing varying proportions of uranyl sulphate and ammonium aurintricarboxylate were

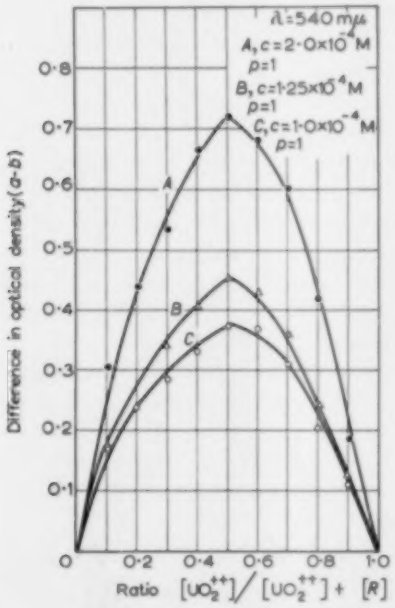

FIG. 1.

prepared and the optical densities at different wavelengths measured with the spectrophotometer. In each mixture, λ_{max} was observed in the same spectral region of 540 mμ, showing that the nature of complex species in all the mixtures are identical. It is, hence, concluded that only one complex is formed in the system investigated here.

[9] W. C. VOSBURGH and G. R. COOPER, *J. Amer. chem. Soc.* **63**, 437 (1941); **64**, 1630 (1942).

Stoicheiometry of the components

The composition of the complex was determined by JOB's method of continuous variation.[10] The total volume in each case was 50 ml. The optical densities were measured at the region of maximum absorption, i.e. at 540 mμ. Various concentrations of the reactants were used and the results are represented graphically in Figs. 1–3. In the figures, the difference of optical density of the mixture and that which would be shown by the chelating agent alone, if no chelation occurred, is plotted against the composition of the mixture. It may be noted that uranyl ion does not show any absorption at the dilutions employed and in the spectral region of observation.

The results of electrical conductance studies are plotted in Figs. 4 and 5. Here too, the difference in observed conductance of the mixture and that expected to be shown in case of no reaction between the metal ion and the reagent, is plotted against the composition of the mixtures.

The pH of the mixtures were between 5·0 and 6·0, and it was already seen that the colour of the reagent is not affected by this change in pH.

In the legends to the figures, c represents the concentration of uranyl solution and c' that of the chelating agent, i.e. $p = c'/c$.

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DISCUSSION

The results presented in this paper establish that the peaks in the curves occur at a ratio of 1 : 1 of the reactants, showing that the chelate is formed between one part each of uranyl ion and the chelating agent.

We have followed the method described by us earlier,[11] for the calculation of formation constant, from optical density data. The method of continuous variation is employed and the optical densities of mixtures of various compositions measured at a fixed wavelength. The observed optical density is plotted against $[M]/([M] + [R])$, ($[M]$ = concentration of the metal ion and $[R]$ that of the chelating agent). In Fig. 6, such a graph is shown for the system investigated. At the concentrations and wavelengths employed, uranyl ion has no absorption and the colour of the mixtures is due to the reagent and chelate only. Hence, with the progressive addition of metal ions. $[R]$ decreases and in the descending portions of the curves, where metal ions are in large excess, the whole of the reagent may be taken to be bound up in the complex. Therefore, in this portion of the curve, the contribution of the free chelating agent to the optical density of the system is negligible. The observed optical density, hence, may be regarded as due to the colour of the chelate formed. Thus in Fig. 6, in the curves A, B and C, where the optical densities are identical (say 0·3), the respective amounts of the complex may be taken to be equal.

In a complex-forming equilibrium of the type:

$$mA + nB \rightleftharpoons A_mB_n$$

if $m = n = 1$, the formation constant K, is given by,

$$K = \frac{x}{(a - x)(b - x)} \qquad (1)$$

[10] P. JOB, *C. R. Acad. Sci., Paris* **180**, 928 (1925); *Ann. chim.* (10) 9, 113 (1928); (**11**) 6, 97 (1936).
[11] A. K. MUKHERJI and A. K. DEY, *J. Ind. chem. Soc.* **34**, 461 (1957).

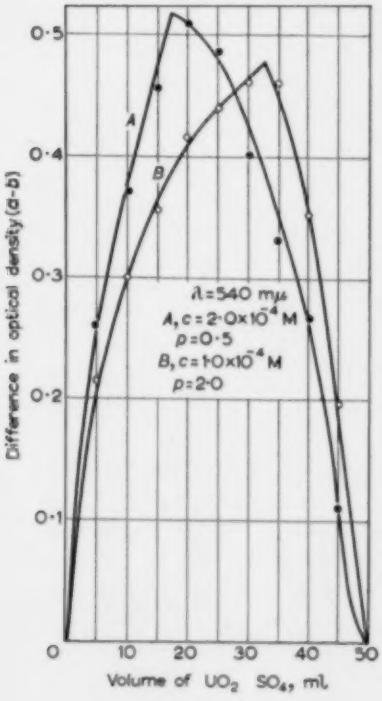

FIG. 2.

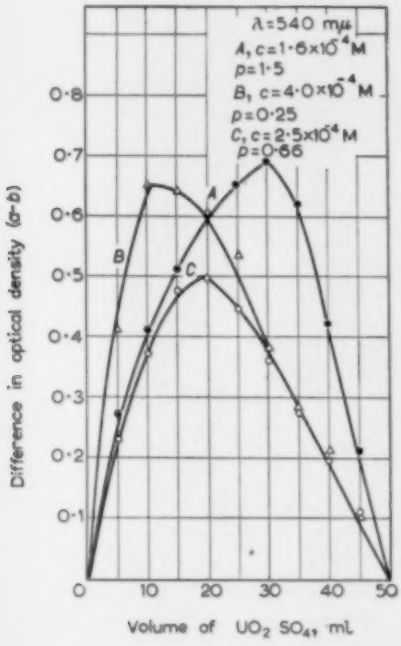

FIG. 3.

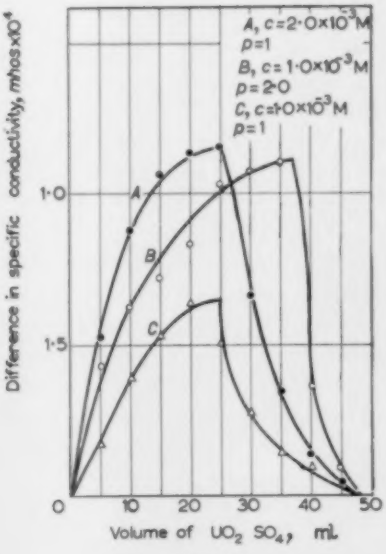

FIG. 4.

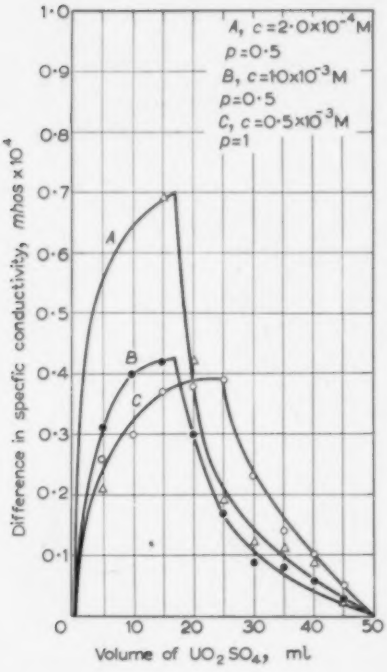

FIG. 5.

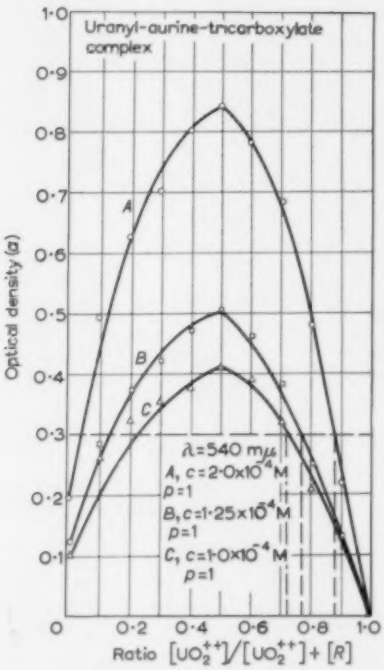

FIG. 6.

where x = concentration of the complex at equilibrium, and a and b are the initial concentrations of the metal ion and the chelating agent, respectively.

Taking two concentrations a_1, a_2 and b_1, b_2 of the reactants, having the same value of x, i.e. identical optical density, we have,

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)} \tag{2}$$

or

$$x = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)}. \tag{3}$$

The values of a and b are read from the curves and the value of x is known from equation (3). The value of K can then be calculated from equation (1).

The formation constant of the uranyl—ammonium aurintricarboxylate chelate, as calculated by the above procedure, is $5{\cdot}9 \pm 0{\cdot}5 \times 10^4$.

The free energy of formation ΔF^0, of the chelate has been calculated with the help of the relation between ΔF^0, R the gas constant, T the absolute temperature and K the formation constant, the relation being

$$\Delta F^0 = -RT \ln K. \tag{4}$$

The free energy of formation of the chelate investigated here is found to be $-6{\cdot}51 \pm 0{\cdot}05$ kcal at 25°C.

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OXALATO COMPLEXES OF Co(II) AND Co(III)

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(*Received* 12 *November* 1957)

Abstract—The results of various chemical and physical–chemical studies on the oxalato complexes of di- and tri-valent cobalt are reported. Evidence is presented for a Co(II) trioxalato complex with a dissociation constant of ca. 0·1, and that the complex known as Durrant's salt, of empirical formula $K_2Co(C_2O_4)_2(OH)(H_2O)$, has a bridged and probably binuclear structure. Durrant's salt is formed by the action of two-electron, oxygen carrying oxidants, such as hydrogen peroxide and hypochlorite, on solutions of Co(II) in excess oxalate. The one electron oxidant, Ce(IV) gives, instead, $Co(C_2O_4)_3^{-3}$. Possible explanations of the specificity of various oxidants are discussed.

The kinetics of the thermal decomposition of $Co(C_2O_4)_3^{-3}$ and of the exchange with Co(II) are reported on, and a common mechanism is proposed, involving the oxalate radical ion as intermediate.

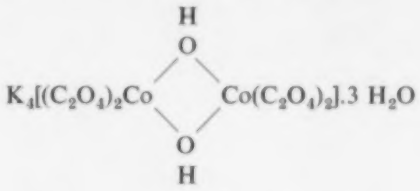
THE initial purpose of the investigations reported here was to study the rates and nature of redox reactions involving oxalato complexes of cobalt, with particular reference to comparisons between atom transfer and electron transfer processes. In order better to understand the mechanisms of the redox reactions involved, however, it became necessary to investigate separately the nature of these complexes.

The species $Co(C_2O_4)_2^{-2}$ is well known, and a dissociation constant of 2×10^{-7} has been reported.[1] Since at least two different Co(III) complexes result from the oxidation of solutions containing Co(II) and oxalate ions, it was important to know whether any higher Co(II) oxalato complexes existed. The solid $(NH_4)_4Co(C_2O_4)_3 \cdot 6H_2O$ has been reported,[2] but no direct evidence was found in the literature for the aqueous species $Co(C_2O_4)_3^{-4}$.

Turning to Co(III) complexes, the species $Co(C_2O_4)_3^{-3}$ is again well known. Its preparation,[3] resolution,[4,5] rate of racemization,[5] rate of thermal[6] and photochemical[7] decomposition, rate of exchange with oxalate ion,[8] absorption spectrum,[9] and redox behaviour[10] have been reported. In contrast to the Cr(III) family of oxalato complexes, the only other Co(III) complex known is

[1] J. E. BARNEY, W. J. ARGERSINGER and C. A. REYNOLDS, *J. Amer. chem. Soc.* **73**, 3788 (1951).
[2] F. EPHRAIM, *Ber. dtsch. chem. Ges.* **42**, 3850 (1909).
[3] J. C. BAILER, JR. and E. M. JONES, *Inorganic Syntheses* (Edited by H. S. BOOTH) Vol. I, p. 37. McGraw-Hill, New York (1939).
[4] W. KAHN and K. BEIN, *Z. phys. Chem.* B **24**, 335 (1934).
[5] E. BUSHRA and C. H. JOHNSON, *J. chem. Soc.* 1937 (1935); C. H. JOHNSON, *Trans. Faraday Soc.* **31**, 1612 (1935).
[6] J. VRANEK, *Z. Elektrochem* **23**, 336 (1939); J. KRANIG, *Ann. Chim.* **11**, 44 (1923).
[7] F. M. JAEGER and G. BERGER, *Proc. Acad. Sci. Amsterdam* **23**, 84 (1920); W. V. BHAGWAT and N. R. DHAR, *Z. anorg. Chem.* **197**, 18 (1931); R. TSUCHIDA, A. NAKAMURA and M. KOBAYASHI, *J. chem. Soc. Japan*, **56**, 1335 (1935); I. G. MURGULESCU, *Bul. Soc. stiinte cluj.* **8**, 193, (1935).
[8] F. A. LONG, *J. Amer. chem. Soc.* **63**, 1353 (1941).
[9] G. SPACU, J. G. MURGULSCU and M. VANCEA, *Z. anorg. Chem.* **220**, 1 (1934). See ref. (6).
[10] I. M. KOLTHOFF and J. J. LINGANE, *Polarography* Vol. II p. 485. Interscience New York (1952).

a species which has variously been stated to be $[K_2Co(C_2O_4)_2(H_2O)_2]_2O$,[11] $K_2[Co(C_2O_4)_2(OH)(H_2O)]$,[9,12] and the bridged species,[13]



I

EXPERIMENTAL

Co(II) *oxalato complexes.* Attempts to confirm the existence of the reported[2] $(NH_4)_4Co(C_2O_4)_3 \cdot 6\ H_2O$ were uniformly unsuccessful, as were also attempts to prepare the corresponding beryllium and sodium salts. Concentrated solutions containing an oxalate to cobalt ratio of 2·5 or more deposit reddish brown crystals, but, as reported by DEAKIN *et al.*,[14] analysis showed the solid to be $K_2Co(C_2O_4)_2 \cdot 6\ H_2O$.

The titration studies were carried out at 20°C by the addition of 1·70 M hydrochloric acid to solutions 1·2 M in sodium oxalate and containing various formalities of added cobaltous nitrate. The amount of bound oxalate and the average ligand number, n, were then calculated from the extent to which the plots of pH vs. amount of added acid were shifted relative to the curve for sodium oxalate solution alone. It was assumed that in the pH range involved, from 5·3 to 4·1, the only proton acceptor was oxalate ion.

The spectrophotometric studies were carried out with 0·0031 M cobaltous nitrate solutions containing increasing concentrations of added sodium oxalate. Ten centimetre cells, and a Beckman Model DU spectrophotometer were used, and a wavelength of 534 mμ, corresponding to the visible absorption band. With increasing oxalate concentration, the maximum shifted slightly towards longer wavelengths, and increased considerably in intensity.

Durrant's salt. Some difficulty was encountered with the preparation of (I) as described by DURRANT,[11] but the following modification was effective. One hundred and sixty-six grams of potassium oxalate monohydrate were dissolved in 400 ml of water and 140 g of air dried cobaltous oxalate were then added. The suspension was boiled gently for 30 min and the small excess of cobaltous oxalate filtered off. To the resulting deep red filtrate 300 ml of 30 per cent hydrogen peroxide was added gradually, maintaining the temperature between 40° and 50°C; it was necessary to add ice at intervals. A suspension of fine crystals developed, and on cooling and filtering, 124 g of deep green product was obtained. If the oxalate to cobalt ratio employed was made 3/1, the yield dropped by about one third. It is likely that varying amounts of $K_3Co(C_2O_4)3$ were formed, but, being quite soluble, this compound remained in solution.

Sodium hypochlorite oxidation also gave Durrant's salt. Thus 0·001 M hypochlorite (adjusted to pH 7) gave complete oxidation of 0·001 M Co(II) in 0·05 M oxalate in 10 sec at 5°C. With 1·5 M oxalate, only partial oxidation occurred in 15 sec. The identity of the product was determined from the absorption spectrum.

Aqueous Durrant's salt undergoes a thermal decomposition to Co(II) and carbon dioxide, especially in acid solution. Measurement of the amount of evolved gas showed that 1·03 moles of carbon dioxide were produced per mole of cobalt, in accord with the equation:

$$\underset{\text{I}}{(\text{I})} \rightarrow 2Co^{++} + 2CO_2 + \underset{\text{II}}{3C_2O_4^{--}} + 2OH^-$$

Solid Durrant's salt undergoes the same thermal decomposition at 100°C, with a colour change to magenta. The magenta product effervesces on the addition of water, due to the escape of trapped

[11] R. G. DURRANT, *J. chem. Soc.* 1781 (1905).
[12] A. WERNER, *Liebigs Ann.* **406**, 271 (1914).
[13] E. PERCIVAL and W. WARDLAW, *J. chem. Soc.* **135**, 2628 (1929).
[14] S. DEAKIN, M. SCOTT and B.D. STEELE, *Z. phys. Chem.* **69**, 123 (1909).

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carbon dioxide. A particular sample of Durrant's salt was found to lose 11 per cent of its weight on heating, and analysis of the residue gave 19·3 per cent Co, as determined by the method of CARTLEDGE and NICHOLS,[15] and 41·3 per cent oxalate, as determined by permanganate titration. This corresponds to 17·2 per cent Co and 36·7 per cent oxalate on correcting for the 11 per cent weight loss, and to 17·2 per cent Co and 49·6 per cent oxalate in the original complex, assuming that before decomposition one additional mole of oxalate was present. The closest empirical formula would be $K_3Co(C_2O_4)_2(OH)(H_2O)$(Co, 16·9 per cent oxalate, 50·7 per cent), but the compound could be either this or the binuclear formulation with two waters of crystallization.

The absorption spectrum of aqueous Durrant's salt shows a maximum at 600 mμ(ε = 115), a minimum at 500 mμ(ε = 20), a marked shoulder at 415 mμ(ε = 175), and a maximum at 290 mμ (ε = 1500). The barium and potassium salts are only moderately soluble; a saturated solution of the latter in 5 M potassium nitrate at −10°C is 0·01 M. No insoluble salts were found, although a number of transition metal ions were tested; the complex is not soluble in organic solvents.

Potassium trisoxalatocobaltate (III). The compound $K_3Co(C_2O_4)_3$ was prepared according to JAEGER and SORENSEN (see ref. 3), and vacuum dried. The dry complex, like Durrant's salt, undergoes a thermal decomposition to carbon dioxide and Co(II), but more slowly. A sample heated for 90 min at 100°C lost 11 per cent in weight, turning magenta in colour, and evolving trapped carbon dioxide on the addition of water. On analysis, the magenta product contained 14·1 per cent Co and 50·7 per cent oxalate, and, on correcting for the weight loss and assuming 1 mole of carbon dioxide evolved per mole of cobalt, the original preparation contained 12·6 per cent Co and 54·5 per cent oxalate: Calculated for $K_3Co(C_2O_4)_3 \cdot 2{\cdot}2H_2O$: 12·3 per cent Co, 54·8 per cent oxalate.

The standard method of preparation makes use of lead dioxide as oxidant; it was found that Ce(IV) could also be used. Thus for a solution 1 M in potassium oxalate, 0·4 M in cobaltous nitrate, and 0·25 M in ceric ammonium sulphate, oxidation was nearly complete in 1 hr at room temperature. Removal of the cerous oxalate precipitate which was formed left a clear green solution from which the trioxalate complex could be precipitated by the addition of ethanol. The reaction was slower with solutions 0·1 M in cobaltous nitrate and several tenths M in potassium oxalate.

The absorption spectrum of the aqueous complex differs from that of Durrant's salt in that there is a minimum at 360 mμ(ε = 56). Other features are a maximum at 605 mμ(ε = 175), a minimum at 500 mμ(ε = 12), a maximum at 425 mμ(ε = 230), and a maximum at 285 mμ(ε = 1450).

Exchange and thermal decomposition studies. The procedure for the exchange runs with the trioxalate complex consisted of preparing a solution containing the desired formalities of cobaltous nitrate and potassium oxalate, then adding a small amount of ^{60}Co(II) tracer, and, finally, the desired amount of aqueous $K_3Co(C_2O_4)_3$. Separation was accomplished by precipitating the Co(II) as the ferrocyanide salt. To make the separation radiochemically complete, it was necessary to add inactive cobaltous nitrate to the supernatant and wash out the remaining radiocobalt as a second ferrocyanide precipitate. The concentration of complex was determined spectrophotometrically, and its radioactivity by precipitating the cobalt as the sulphide and counting the solid by means of a scintillation counter.

The same general procedure was employed in the case of Durrant's salt. Separation, however, was accomplished by the addition of solid potassium nitrate and cooling to −5°C, under which conditions most of the complex precipitated as the potassium salt.

RESULTS AND DISCUSSION

Evidence for a trioxalate complex of Co(II). As described in the preceding section, the presence of Co(II) shifted the pH titration curves for sodium oxalate solutions. Over the pH range of the titration, n was 2·94 ± 0·4, with a slight downward trend as the concentration of free oxalate was reduced by the titration. The n values were not affected by solution non-idealities since they were obtained by comparison of the formalities of added acid to give the same hydrogen ion activity with and without the presence of Co(II). A trioxalate complex is thus indicated, but no attempt was made to estimate its stability constant from the titration because of the uncertainty in activity coefficients. Instead, the following spectrophotometric data were obtained.

[15] G. H CARTLEDGE and P. M. NICHOLS, *Industr. Engng. Chem.* (*Anal.*) **13**, 20 (1941).

The optical density at 534 mμ of a solution of Co(II) rises steadily with increasing oxalate concentration, as shown in Fig. 1. The resulting apparent extinction coefficients were then plotted against the total oxalate concentration, C, and against $1/C$, so as to obtain by extrapolation the values of 9·70 and of 19·3 for the di- and trioxalate complexes, respectively. From these, the fraction, F, of cobalt present as the

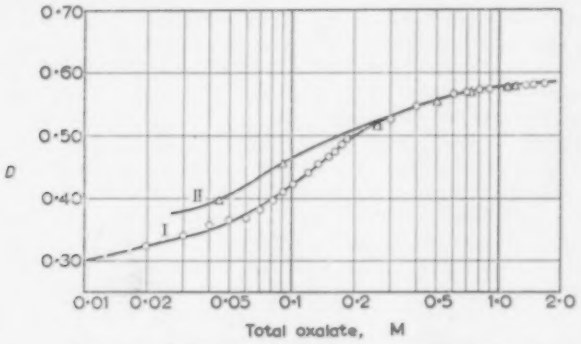

FIG. 1. Ordinate: D Abscissa: Total oxalate, M
Variation of optical density with $K_2C_2O_4$ concentration at constant Co(II) concentration. 10 cm cells, 0·0031 M $Co(NO_3)_2$. ○, no added K_2SO_4; △ added K_2SO_4 up to 0·65 M so as to keep μ as constant as possible. The pH was 7·2 in both cases.

dioxalate species could be calculated for each oxalate concentration. As shown in Table 1, the results were best fitted by taking the dissociation constant to be 0·11.

An attempt was made at keeping ionic strength constant, by adding potassium sulphate as the total oxalate was reduced. This led to curve II in Fig. 1, which corresponds to a smaller K value. Qualitatively, this is the result that would be expected on the basis of activity coefficient effects.

TABLE 1.—SPECTROPHOTOMETRIC DATA ON THE FORMATION OF $Co(C_2O_4)_2^{-4}$

$C_2O_4^{-2}$ (M)	F	Apparent extinction coefficient		
		Calc.[a]	obs.[b]	obs.[c]
1·5	0·070	18·6	18·9	19·9
1·0	0·10	18·3	18·5	18·5
0·5	0·18	17·6	17·9	17·9
0·1	0·52	14·1	13·5	15·0
0·05	0·69	12·4	11·9	13·0
0·02	0·84	10·7	10·5	—

(a) assuming $K = 0·11$
(b) no added K_2SO_4
(c) added K_2SO_4

Durrant's salt. The present investigations provide a qualitative indication that Durrant's salt has the binuclear structure (I) rather than the mononuclear one suggested by WERNER. If the correct formula were $K_2[Co(C_2O_4)_2(OH)(H_2O)]$, then, by analogy with the corresponding Cr(III) species, this should be the salt of an acid of pH ca. 7[16]. Solutions of Durrant's salt, however, are neutral (note the starting

[16] G. E. CUNNINGHAM, R. W. BURLEY and M. T. FRIEND, *Nature, Lond.* **169**, 1103 (1952).

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point in Fig. 2, discussed below), and the pH titration curve showed no indication of the presence of a weak acid. There was evidence, however, that a new species was formed by the addition of acid and that this species was a weak acid of pH about 7. Thus, as shown in Fig. 2, the acid titration curve was not retraced on addition of base, and the product solution showed the beginning of a buffer region at pH 7, beyond which destructive decomposition began to set in. Once acidified, solutions could be titrated back and forth nearly reversibly, but along a path displaced from the one of initial acidification. This displacement corresponded to nearly one equivalent of hydrogen ion per mole of cobalt, but could not be determined accurately since the thermal decomposition of the acidified solutions was rapid.

It might be noted that the alkaline decomposition of the original solution, which

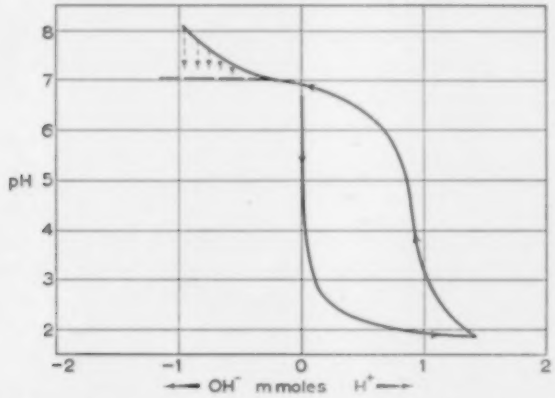


FIG. 2. Ordinate: pH Abscissa: (indicated on the figure)
Acid titration, and back titration of Durrant's salt.
1·76 m moles complex in 150 ml of 0·4 M $NaClO_4$ at −3°C. Titrated with 0·0484 N $HClO_4$, back titrated with 0·0477 N NaOH in 0·4 M $NaClO_4$, under N_2 atmosphere.

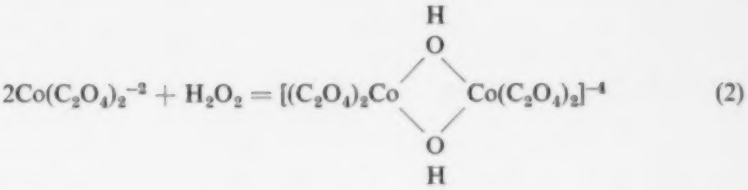
set in at a pH of about 9, and of acidified solution, which set in slightly beyond pH 7, was of a hydrolytic nature involving cobaltic hydroxide formation, while the thermal decomposition of the acidified solution, as well as of the original solution, led to Co(II) and carbon dioxide.

The above titration behaviour cannot be explained on the basis of a mononuclear formulation for Durrant's salt, but can be explained in terms of an acid induced fission of a binuclear species:

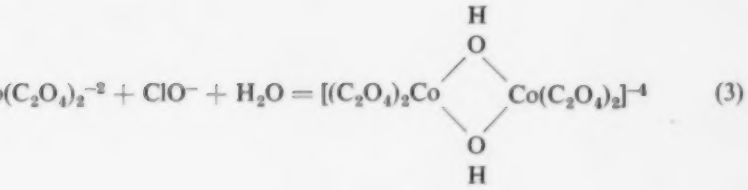
$$[(C_2O_4)_2Co\begin{matrix}H\\O\\O\\H\end{matrix}Co(C_2O_4)_2]^{-4} + 2H^+ + 2H_2O = 2[Co(C_2O_4)_2(H_2O)_2]^{-1}. \quad (1)$$

The pK of the bridged form might be about 9, judging from the pH of incipient decomposition on the direct addition of base to a solution of Durrant's salt, while that of the diaquo product might be about 7, judging from the back-titration curve.

Oxidation of Co(II) *oxalate complexes.* The following reactions were described under EXPERIMENTAL:



$$2Co(C_2O_4)_2^{-2} + H_2O_2 = [(C_2O_4)_2Co \; Co(C_2O_4)_2]^{-4} \quad (2)$$



$$2Co(C_2O_4)_2^{-2} + ClO^- + H_2O = [(C_2O_4)_2Co \; Co(C_2O_4)_2]^{-4} \quad (3)$$

$$Co(C_2O_4)_3^{-4} + Ce(IV) = Co(CEO_4)_3^{-3} + Ce(III). \quad (4)$$

The dioxalato complex is taken to be the reactant in (2) and (3) since Durrant's salt was formed, and its yield decreased with increasing oxalate concentration. The evidence similarly leads to the conclusion that $Co(C_2O_4)_3^{-4}$ is the reactant in (4).

While no experimental information on the detailed kinetics was obtained, it is tempting to suppose that (2) and (3) are atom transfer in type, with oxygen of the oxidant adding to the Co(II) complex; the slowness of the former relative to the latter could be explained as a result of the necessity of breaking the oxygen–oxygen bond in hydrogen peroxide. Moreover, the two atom transfer processes resemble others for cobalt systems[17,18] in being fairly rapid and in giving a product representing an adduct with the oxidizing agent. On the other hand, (4) has the slowness generally observed for Co(II)–Co(III) charge transfer reactions.[19]

Exchange and thermal decomposition studies. Preliminary investigation showed that the exhange of radiocobalt as a Co(II) in oxalate solution with $Co(C_2O_4)_3^{-3}$ was slow and was probably geared to the thermal decomposition which was occurring at a similar rate,

$$2Co(C_2O_4)_3^{-3} = 2Co(C_2O_4)_2^{-2} + C_2O_4^{-2} + 2CO_2. \quad (5)$$

Representative data for the thermal decomposition at 40° and 50°C are shown in Fig. 3, and it is seen that there is a falling off from first order character with time, especially at low free oxalate ion concentrations. The apparent half-lives for the initial portions of Runs 6 and 7, and 10 are 48 and 8·5 hr, respectively, corresponding to a temperature coefficient of 5·7, as compared to the value of 4·6 reported by VRANEK.[6]

By analogy with the mechanism proposed for the photodecomposition,[7] and in

[17] A. W. ADAMSON, *J. Amer. chem. Soc.* **78**, 4260 (1956).
[18] A. W. ADAMSON, *Rec. trav. chim.* **75**, 809 (1956).
[19] A. W. ADAMSON and K. VORRES, *J. inorg. nucl. Chem.* **3**, 206 (1956).

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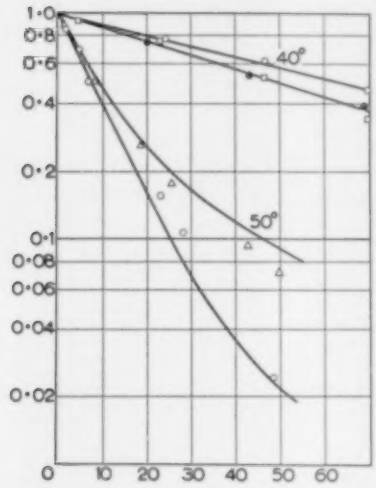

FIG. 3. Ordinate: $B = B/B^0$ Abscissa: Time (hr)
Thermal decomposition of $Co(C_2O_4)_3^{-3}$
40°C: ○, Run 5, $Ox = 0{\cdot}08$ M, $C = 0{\cdot}005$, $B^0 = 0{\cdot}02$ M; □, Run 6, $Ox = 1{\cdot}63$ M, $C = 0{\cdot}04$ M, $B^0 = 0{\cdot}04$ M; ●, Run 7, $Ox = 0{\cdot}08$, $B^0 = 0{\cdot}02$ M. 50°C: △, Run 9, $Ox = 0{\cdot}08$ M, $C = 0{\cdot}005$ M, $B^0 = 0{\cdot}02$ M; ○, Run 10, $Ox = 1{\cdot}63$ M, $B^0 = 0{\cdot}04$ M (Ox denotes $K_2C_2O_4$, C, $Co(NO_3)_2$, and B^0, $K_3Co(C_2O_4)_3$

line with other mechanisms for oxalate reactions,[20,21] it seems reasonable to propose the following scheme:

$$Co(C_2O_4)_3^{-3} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(C_2O_4)_2^{-2} + C_2O_4^{-} \tag{6}$$

$$Co(C_2O_4)_2^{-2} + C_2O_4^{-2} \overset{K}{\rightleftharpoons} Co(C_2O_4)_3^{-4} \quad \text{(rapid equilibrium)} \tag{7}$$

$$Co(C_2O_4)_3^{-3} + C_2O_4^{-} \xrightarrow{k_3} CO(C_2O_4)_2^{-2} + C_2O_4^{-2} + 2\,CO_2. \tag{8}$$

Assuming steady state conditions, the rate law becomes:

$$dB/dt = -\frac{2k_1k_3B^2}{k_2A + k_3B} \tag{9}$$

where A and B denote the concentrations of $Co(C_2O_4)_2^{-2}$ and $Co(C_2O_3)_3^{-3}$, respectively. If it is assumed that the fraction, F, of the Co(II) present as the dioxalato complex is constant, then (9) may be integrated to give:

$$\ln B/B^0 = -\frac{2k_1k_3t}{k_3 - k'_2} + \frac{k'_2D}{(k_3 - k_2)B^0}(B^0/B - 1) \tag{10}$$

where $k'_2 = Fk_2$, and D denotes the total cobalt concentration. The solid lines in Fig. 3 represent the best fit of (10) to the thermal decomposition data *which is also consistent* with the exchange results discussed below.

[20] A. W. ADAMSON, *J. phys. coll. Chem.* **55**, 293 (1951).
[21] H. TAUBE, *J. Amer. chem. Soc.* **70**, 1216 (1948).

The rate of exchange of Co(II) with $Co(C_2O_4)_3^{-3}$ is predicted by the above mechanism to be given by the rate law:

$$dy/dt = \frac{k_1k_1(Bx - Ay) - 2\,k_1k_3By}{k_2A + k_3B} \tag{11}$$

where x and y denote the concentrations of radiocobalt as $Co(C_2O_4)_2^{-2}$ and $Co(C_2O_4)_3^{-3}$, respectively. As is frequently the case with exchange in a reacting system, the integrated form is especially simple if expressed as the variation in specific activity, $S_y(S_y = y/B)$ with degree of reaction. Thus (II) becomes:

$$dS_y/dt = -\frac{k'_2}{2k_3B^2}(x^0 - DS_y) \tag{12}$$

where x^0 denotes the total radiocobalt concentration. Integration then gives

$$\ln(1 - S_y/S_y^{\infty}) = -\frac{k'_2}{2k_3B^0}\left(\frac{B^0}{B} - 1\right) \tag{13}$$

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TABLE 2.—EXCHANGE AND THERMAL DECOMPOSITION FOR $Co(C_2O_4)_3^{-3}$
($T = 50°C$, $B^0 = 0{\cdot}02$ M, Co(II) = 0·005 M, $K_2C_2O_4 = 0{\cdot}08$ M)

Time (hr)	y/x^0	y/y^{∞} [a]	B/B^0
10 (min)	0·004		1·00
2·5	0·063	0·090	0·88
19·5	0·097	0·470	0·26
26·5	0·080	0·59	0·17$_7$
43·5	0·058	0·86	0·094
50·5	0·043	0·86	0·071

[a] $y^{\infty} = x_0B/D$

The exchange and thermal decomposition data are given for Run 9 in Table 2, and the exchange results are plotted in Fig. 4 according to (13). The table illustrates the chief difficulty with the exchange measurement, namely that a maximum of only about ten per cent of the activity appeared in the Co(III) fraction; at short times there was little exchange, while at long times there was little complex remaining. The data for Run 9 are plotted according to (13) in Fig. 4, and the agreement is essentially within the assumed experimental error of one per cent in counting and two per cent in B/B^0 values.

For Run 9, F was within a few per cent of being constant at 0·70; from this value, and the slope for Fig. 4, the ratio k_2/k_3 was found to be 0·40 at 50°C. This value was then used in applying equation (10) to the thermal decomposition data (Runs 9 and 10), and the value of k_1 giving the best fit (solid lines in Fig. 3) was 0·051 hr^{-1}.

It is thus possible to account in detail for both the exchange and the thermal decomposition results on the basis of the common mechanism proposed, and it appears that the alternate exchange path involving a charge transfer between the Co(II) and Co(III) trioxalato ions was unimportant. Roughly, the maximum

specific rate constant for charge transfer would be 0·4 hr^{-1} at 50°C. This value, while small, is consistent with the general slowness of charge transfer processes between Co(II) and Co(III).[19]

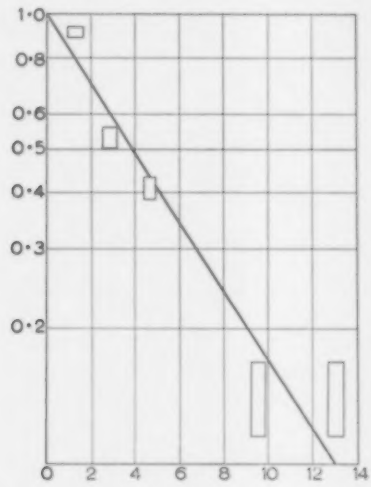

FIG. 4. Ordinate: $1 - S_y/S_y^{\infty}$ Abscissa: $\frac{B^0}{B} - 1$

Exchange between Co(II) and $Co(C_2O_4)_3^{-3}$ in excess oxalate
Data of Run 9; see Table 3.

Returning to the proposed mechanism, there is no conflict with LONG's finding[8] of no exchange between ^{14}C labelled oxalate ion and the trioxalato complex because the rate constants found here are such that appreciable change should not have occurred under his conditions. Racemization is also predicted by the above mechanism, the rate law being:

$$dS/dt = -\frac{k_1 k_2 AS}{k_2 A + k_3 B} \tag{14}$$

where S is proportional to the specific rotation. For solutions containing only $K_3Co(C_2O_4)_3$, (14) predicts an induction period, contrary to observation; moreover, under the conditions of Run 9, the predicted initial apparent first order rate constant for racemization is 0·0033 hr^{-1}, as compared to the far higher value of 0·1 hr^{-1} actually observed.[5] Evidently, LONG's conclusion that only a partial loosening of the oxalate–cobalt bonds is sufficient for racemization is correct.

Some qualitative studies were made of the exchange between radio-cobalt (II) in excess oxalate, and Durrant's salt. McKay plots gave half-lives of ca. 2 hr at 25°C for solutions 0·2 M in sodium oxalate, 0·005 M in cobaltous nitrate, and 0·02 M in Durrant's salt. The plots were not linear, however, and showed an induction period which was decreased if a 2 or 3 hr pre-equilibration was allowed before the introduction of the tracer Co(II). There was, moreover, a small decrease in optical density with time, and a considerable decrease in the amount of Durrant's salt precipitable with potassium nitrate, which indicated that some net reaction, such as (1) was occurring.

Acknowledgement—These investigations were supported in part by contract N6onr23809 between the University of Southern California and the Office of Naval Research.

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 328 to 333. Pergamon Press Ltd., London

TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—V

FURTHER RESULTS FOR THE TETRA- AND HEXAVALENT ACTINIDE NITRATES

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(*Received* 4 *February* 1958)

Abstract—Partition coefficients have been determined (some in earlier papers in this series) for (Th, Np, Pu)$(NO_3)_4$ and (U, Np, Pu)$O_2(NO_3)_2$ at trace concentrations in presence of nitric acid, between a tri-*n*-butyl phosphate (TBP) and an aqueous phase. All are strongly extracted, and all appear to form di-solvates, $M(NO_3)_4 \cdot 2TBP$ and $MO_2(NO_3)_2 \cdot 2TBP$. Extraction generally increases in the order Th < Np(IV) < Pu(IV), but the series U(VI) > Np(VI) > Pu(VI) shows the reverse trend.

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RESULTS have already been published in this series for the extraction of traces of thorium,[1] plutonium(IV) and plutonyl[2] nitrates by tri-*n*-butyl phosphate (TBP) from aqueous nitric acid. The present paper covers most of the remaining tetra- and hexavalent actinide nitrates, namely uranyl, neptunium(IV) and neptunyl nitrate. In most cases we have used a 19% v/v solution of TBP in kerosene as the extracting agent.

It is somewhat surprising that accurate data for uranyl nitrate at trace concentrations in the presence of nitric acid have not hitherto been available, despite extensive use of TBP for the extraction of this species. It was indeed in relation to uranyl nitrate that interest in TBP as an extracting solvent was first aroused, and under many conditions uranyl nitrate remains, with one exception, viz. cerium(IV)[3] nitrate, the most extractable nitrate yet studied.

EXPERIMENTAL

The general techniques used were described in Part I[4] of this series.

Uranium was studied first with natural uranium and later with $1{\cdot}6 \times 10^5$ year ^{233}U, the initial concentration being 0·5–1 g/l. Natural uranium was analysed colorimetrically by either the peroxide or the thiocyanate method, and ^{233}U by α-counting. The last-named method was the most sensitive; indeed it was not possible to use natural uranium at the concentration level in question, to measure partition coefficients widely different from unity.

The ^{233}U usually contains the relatively short-lived (74 year) ^{232}U, which may make an appreciable contribution to its α-activity. In our case there was a 0·6 per cent contribution. This would not matter, were it not for the α-emitting decay products of ^{232}U, which slowly grow in and usually remain behind in the aqueous phase in TBP extractions. In cases where most of the uranium passes into the TBP phase, the effect on the measured partition coefficient can be serious, e.g. if there is 1 per cent of inextractable material, a true partition coefficient (organic/aqueous) of 32 is reduced to an apparent coefficient of 24 (equal volume extractions). It was therefore necessary to purify the ^{233}U

(1) E. HESFORD, H. A. C. MCKAY and D. SCARGILL, *J. inorg. nucl. Chem.* **4**, 321 (1957).
(2) G. F. BEST, H. A. C. MCKAY and P. R. WOODGATE, *J. inorg. nucl. Chem.* **4**, 315 (1957).
(3) T. V. HEALY, Private communication.
(4) K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. inorg. nucl. Chem.* **4**, 100 (1957).

by a solvent extraction cycle immediately before use. The purified material contained <0·02 per cent of impurities by α-counts, a negligible proportion. This was shown by extracting 97 per cent of the uranium and pulse-analysing the α-particles from the residual material; <0·5 per cent of the counts were from elements other than uranium.

If ^{233}U itself were used for the experiments, errors due to its decay products would be proportionately more serious, and would indeed be difficult to reduce to negligible dimensions.

Neptunium was studied with the aid of the $2{\cdot}2 \times 10^6$ year α-emitter ^{237}Np. Previously DAWSON *et al.*[5] had used ^{239}Np, which is a 2·3 day β-emitter, but their results could not be repeated exactly. At the tracer concentrations at which ^{239}Np must be used, the chemical state of the neptunium, and especially its state of oxidation, is presumably very susceptible to trace impurities. Nevertheless, the work of DAWSON *et al.*[5] provides general confirmation of the results reported here.

The precautions taken in handling the ^{237}Np, to ensure that it was completely in either the IV- or the VI-state, have been described by BEST *et al.*[6] in connexion with dibutyl carbitol extractions. It proved rather easier to obtain consistent results with TBP than with dibutyl carbitol, presumably because there was less interference by solvent decomposition products.

Plutonium was studied with 24,300 year ^{239}Pu admixed with higher isotopes. It was oxidized to the VI-state by means of ozone in 0·5–1 M nitric acid, and residual plutonium(IV) was removed by passage through an anion resin column (Deacidite FF) in 7 M nitric acid. The plutonium was then extracted into TBP in presence of a trace of bromate as a holding oxidant, and partition coefficients were determined by back extraction from this TBP solution. Successive back extractions yielded consistent results. We consider that the uncertainty in the earlier Harwell work,[2] as to whether the plutonium was fully oxidized to the VI-state, has now been removed.

RESULTS AND DISCUSSION

Uranyl nitrate

Our partition coefficient measurements at varying TBP concentration (0·5–4% v/v TBP in kerosene) but constant aqueous phase (5 M nitric acid) have already been published[7]. They follow a square law very closely, indicating the formation of a di-solvate, $UO_2(NO_3)_2{\cdot}2TBP$, whose existence is supported by several other lines of evidence[8]. This is valuable from the point of view of validating the TBP dilution method of determining solvation numbers.

Fig. and Table 1 show how the extraction of traces of uranyl nitrate varies with the nitric acid concentration. The only comparable results are those of DUNCAN and HOLBURT[9] for 20% TBP in kerosene, and of SATO[10] for 19% TBP in kerosene. SATO, however, used an initial uranium concentration of 5 g/l. It would be expected that DUNCAN and HOLBURT's results would lie a little above ours and SATO's, since they apply to a slightly higher TBP concentration, but in fact they are a little lower, expecially in the neighbourhood of the maximum. This suggests the presence of ^{232}U decay products (see above) in their material, and they have since stated that there may have been up to 0·5 per cent of such impurities (by α-counts).

In spite of this criticism we consider DUNCAN and HOLBURT's results sufficiently good to help to verify an assumption made throughout the present series of papers, the assumption namely that metal nitrate concentrations up to about 1 g/l. can be treated as trace concentrations. The justification for this has been that, in effect, such concentrations are small in comparison with those of the major constituents

[5] J. K. DAWSON, (Miss) R. ELLIOTT and H. A. C. MCKAY, *AERE/C/R*-1117 (1953).
[6] G. F. BEST, E. HESFORD and H. A. C. MCKAY, *Proc. int. Union pure and appl. Chem.* In press.
[7] H. A. C. MCKAY, *Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, P/441. United Nations (1956); *Progr. nucl. Energy* **1**, 122 (1956).
[8] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).
[9] A. DUNCAN and G. A. HOLBURT, *U.K.A.E.A. Report IGR-TN/W.*055 (1956).
[10] T. SATO, *J. inorg. nucl. Chem.* **6**, 334 (1958).

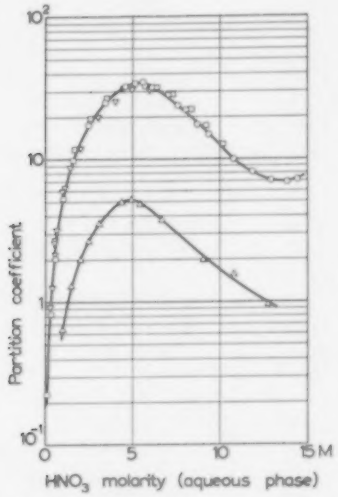

FIG. 1.—The extraction of uranyl nitrate by TBP
△ Our data (4.8% TBP in kerosene)
○ Our data (19% TBP in kerosene)
□ SATO[10] (19% TBP in kerosene 5 g U/l. initially)
▽ DUNCAN and HOLBURT[9] (20% TBP in kerosene)

of the system (nitric acid, water, TBP etc.). In the uranyl nitrate case, DUNCAN and HOLBURT have carried out several series of experiments in which they varied the uranium concentration from about 0·0002 to 0·5 g/l., keeping everything else fixed, and they were unable to detect any change in the partition coefficient. This establishes experimentally that 0·5 g/l., at least, can be treated as a trace concentration and eliminates the possibility of uranyl nitrate reacting with any other trace constituent of the system, or forming polynuclear species under the conditions in question.

Neptunium(IV) *and neptunyl nitrates*

DAWSON *et al.*[5] obtained a square law dependence for the partition coefficients of both neptunium(IV) and neptunyl nitrates as a function of TBP concentration, indicating the formation of $Np(NO_3)_4 \cdot 2TBP$ and $NpO_2(NO_3)_2 \cdot 2TBP$. As this is so much what we should expect by analogy with similar elements, we have not thought it worth while to repeat the work using ^{237}Np.

Fig. 2 and Table 1 give our results for the extraction of traces of the two neptunium nitrates as a function of the acidity. The broken curves show the earlier results of DAWSON *et al.*; it may be suggested that their neptunium(IV) was contaminated with the less extractable neptunium(V) at low acidities, and their neptunium(VI) with neptunium(V) at high acidities. Some Oak Ridge results,[11] with a different TBP concentration and diluent, are also shown in Fig. 2. Having regard to the different conditions they seem in reasonable relation to ours.

Plutonyl nitrate

The new results for plutonyl nitrate agree quite well with those of BEST *et al.*[2] except that the maximum is less flattened (Fig. 3 and Table 1). The change, such as

[11] G. W. PARKER, Private communication.

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TABLE 1

HNO_3 conc. (aq.)	Partition coeff. (org./aq.)
$UO_2(NO_3)_2$, 4·8% TBP	
1·03	0·628
1·50	1·30
2·02	1·97
2·49	2·66
3·06	3·52
4·42	4·96
4·92	5·08
5·42	4·85
6·68	3·80
9·07	1·97
10·8	1·58
12·8	0·96
$UO_2(NO_3)_2$, 19% TBP	
0·137	0·227
0·32	0·832
0·60	2·07
1·05	5·30
1·62	9·73
2·50	17·7
3·50	25·6
4·58	32·0
5·09	34·2
5·52	35·0
5·56	33·6
6·01	32·4
7·06	28·4
7·57	24·0
8·07	22·8
8·73	17·5
9·37	15·2
10·8	10·1
11·9	8·19
12·9	7·19
13·8	6·95
14·4	7·27
$PuO_2(NO_3)_2$, 19% TBP	
0·50	0·286
1·10	0·750
2·10	1·77
2·80	2·22
4·07	2·87
5·03	3·16
5·77	3·38
6·01	3·57
6·76	3·33
7·03	3·27
$PuO_2(NO_3)_2$, 19% TBP—*continued*	
8·08	2·90
9·28	2·27
10·6	1·99
11·1	1·86
12·6	1·71
13·7	1·86
$Np(NO_3)_4$, 19% TBP	
0·78	0·29
1·28	0·54
1·89	0·88
2·14	1·01
2·67	1·67
4·40	3·15
5·77	4·68
7·34	6·68
7·36	6·85
8·26	6·53
9·40	5·76
10·1	4·65
$NpO_2(NO_3)_2$, 19% TBP	
0·44	0·964
0·75	1·84
1·19	3·66
2·05	6·68
3·17	9·44
4·12	11·2
4·65	12·0
5·05	11·4
5·20	11·3
5·52	11·0
5·90	10·2
6·00	9·48
6·60	9·61
7·10	8·87
7·94	7·34
8·09	7·38
8·92	5·37
9·32	5·11
9·83	4·95
10·05	4·54
10·6	3·53
11·2	3·63
12·6	2·65
13·3	2·69
13·9	2·60
14·1	2·89

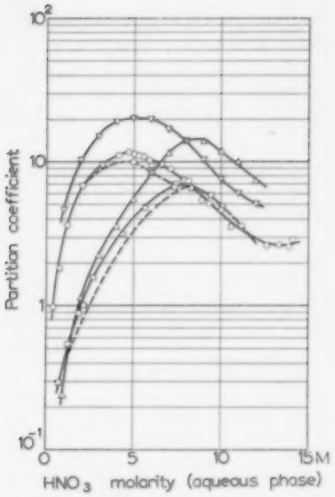

FIG. 2.—The extraction of neptunium(IV) and neptunyl nitrates by TBP
○ Our data, $Np(NO_3)_4$ (19% TBP in kerosene)
□ Our data, $NpO_2(NO_3)_4$ (19% TBP in kerosene)
▽ PARKER,[11] $Np(NO_3)_4$ (30% TBP in Amsco)
△ PARKER,[11] $NpO_2(NO_3)_2$ (30% TBP in Amsco)
– – – DAWSON *et al.*[5] under similar conditions to our present data.

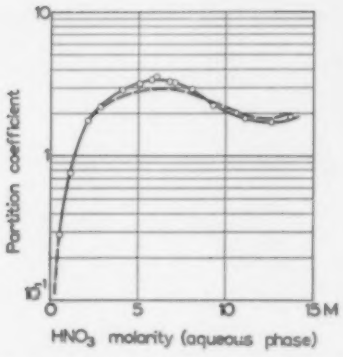

FIG. 3.—The extraction of plutonyl nitrate by TBP
○ Our data (19% TBP in kerosene)
– – – BEST *et al.*[6] under similar conditions to our present data.

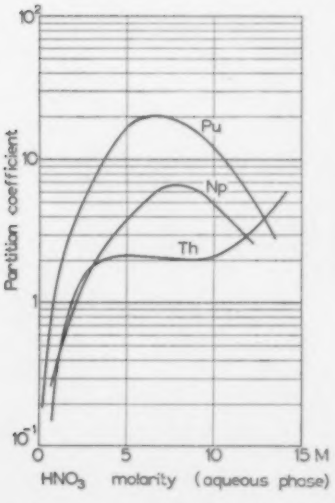

FIG. 4.—The extraction of the tetravalent actinide nitrates by 19% TBP in kerosene.

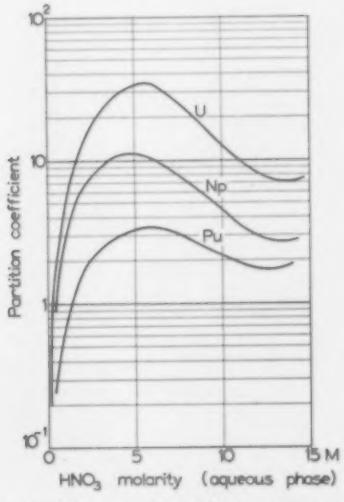

FIG. 5.—The extraction of the hexavalent actinide nitrates by 19% TBP in kerosene.

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it is, is in the opposite direction to what would be expected if the earlier work was affected by the presence of plutonium(IV).

The tetra- and hexavalent actinide nitrate series

It has now been shown that all the nitrates in question form di-solvates, $M(NO_3)_4 \cdot 2TBP$ and $MO_2(NO_3)_2 \cdot 2TBP$.

Figs. 4 and 5 compare the new results at varying acidities with those previously reported for the other actinides. It will be seen that all these elements are strongly extracted by TBP in both the IV- and the VI-valent states, and that they all give similar curves when partition coefficients are plotted against acidity, with a partial exception in the case of thorium. A general explanation of the shapes of the curves has been given by HESFORD and MCKAY.[12]

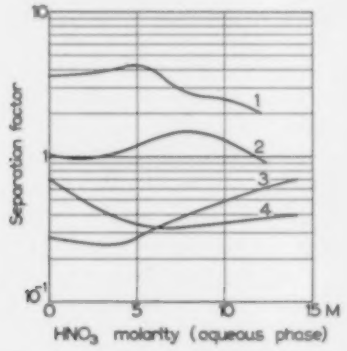

FIG. 6.—Separation factors (distribution coefficient ratios).

1 $D_{(PuIV)}/D_{Np(IV)}$

2 $(D_{Np(IV)}/D_{Th})^{1/3*}$

3 $D_{Pu(VI)}/D_{Np(VI)}$

4 $D_{Np(VI)}/D_{U(VI)}$

* The cube root has been taken because three steps in the Periodic Table are involved.

In the tetravalent series, extractability generally increases with atomic number, Z, but in the hexavalent series it decreases; the latter is an unusual trend. The steps in the series may be large and are far from regular. There is little or no sign of the linear relation between log (partition coefficient) and Z which holds so well among the lower lanthanides.[13]

Separation factor (partition coefficient ratio) curves are given in Fig. 6. These again bring out the irregularity of the steps from one element to another.

[12] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).
[13] D. F. PEPPARD, J. P. FARIS, P. R. GRAY and G. W. MASON, *J. phys. Chem.* **57**, 294 (1953).

J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 334 to 337. Pergamon Press Ltd., London

THE EXTRACTION OF URANYL NITRATE FROM NITRIC ACID SOLUTIONS BY TRIBUTYL PHOSPHATE

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Abstract—The effects of nitric acid concentration, uranyl nitrate concentration, and temperature were investigated in order to determine the optimum conditions for the extraction of uranyl nitrate from nitric acid solutions by TBP. It is apparent from the results that greater than 97 per cent extraction is obtained when uranyl nitrate solution of less than 10 g/l. concentration and containing 6 M HNO_3 is extracted with 19 per cent TBP in kerosene at a temperature of less than 20°C.

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SOLVENT extraction processes for inorganic salts have been rapidly developed in recent years. Many solvents have been tried. Of these, great interest is at present being shown in tributyl phosphate (TBP). The extraction of inorganic nitrates by TBP has been studied by many research workers,[1,2] but comparatively little has been published on uranyl nitrate. In this paper, therefore, an account is given of the investigation of some factors affecting the extraction of uranyl nitrate from nitric acid solution in order to determine the optimum conditions.

EXPERIMENTAL

When 100 per cent TBP is used as the extraction solvent, separation of the organic and aqueous phases is difficult because the specific gravity of TBP is near to that of water. To make the separation easier it is usual to regulate the specific gravity with diluent. However, the presence of large proportions of diluent has the effect of decreasing the solubility of water in TBP, as shown by ALCOCK *et al.*,[2] and this would probably affect the transfer of inorganic salt from aqueous phase to organic phase. The diluent most frequently employed is kerosene, and a concentration of TBP of from 20 to 40 per cent is most widely used for the extraction of inorganic salts.[1-3]

The TBP was purified with 0·1 N sodium hydroxide solution exactly as described by ALCOCK *et al.*,[2] and well washed with water. For this present study 20 volumes of water-saturated TBP was made up to 100 volumes with kerosene as diluent. This solution, because of the water content of the TBP, corresponded in TBP/kerosene ratio to one of 19 volumes of dry TBP made up to 100 volumes with kerosene, and will be referred to as "19 per cent TBP". The kerosene used was such that 25 per cent distilled between 180° and 200°C. The uranyl nitrate used was twice purified by extraction with 19 per cent TBP, being backwashed into water, and it contained 9·4 per cent moisture, as for $UO_2(NO_3)_2 \cdot 6H_2O$.

The extractions were carried out by the following procedure. 50 cm^3 each of solvent and uranyl nitrate solution were put into 100 cm^3 stoppered conical flasks and stood for 30 min in a water bath, thermostated at the required temperature. Then after shaking for 5 min the partition coefficient and the percentage extracted were determined. The partition coefficient is given by the ratio of the

[1] For example, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vols. 7 & 9. United Nations (1956); T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956); K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. inorg. nucl. Chem.* **4**, 100 (1957); L. I. KATZIN, *Ibid.* **4**, 187 (1957).

[2] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).

[3] D. F. PEPPARD, G. W. MASON and L. J. MAIER, *J. inorg. nucl. Chem.* **3**, 215 (1956).

equilibrium concentration in the organic phase to that in the aqueous phase.[4] The percentage extracted is expressed as $100x_1/x$, where x is the concentration of uranyl nitrate contained in the aqueous phase before extraction, and x_1 is that in the organic phase after extraction. Uranium was determined gravimetrically as follows: the uranyl nitrate in the organic phase was back-extracted with ammonium carbonate, the carbonate driven out by boiling, and ammonium diuranate completely precipitated with ammonium hydroxide solution and weighed as U_3O_8 after calcination.

RESULTS AND DISCUSSION

Effect of nitric acid concentration. In order to determine the optimum concentration of nitric acid which acts as salting out agent, extraction of 5 g/l. uranyl nitrate solution was carried out with 19 per cent TBP at 20°C with varying concentrations of nitric acid. The results, plotted in Fig. 1, show that the partition coefficient of uranium is a maximum at about 6 M initial nitric acid concentration.

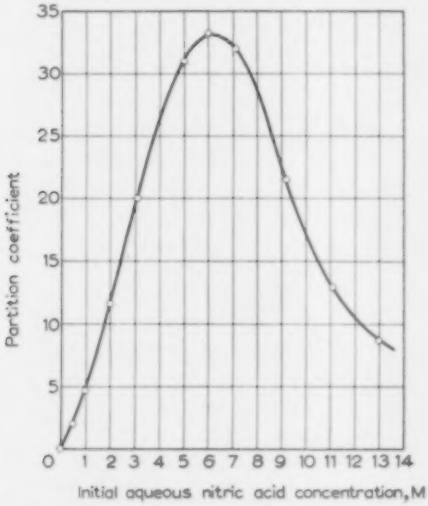

FIG. 1.—Effect of nitric acid concentration upon the extraction of uranyl nitrate by 19 per cent TBP in kerosene

Also, the partition of nitric acid in these solutions was investigated, since a compound such as HNO_3, TBP[5] is formed by the combination of nitric acid and TBP. The direct titration of acidity in the organic phase presented difficulty, however, because the greater proportion of the uranium is present in this phase and its precipitation at about pH4 would interfere. Consequently the acidity of the organic phase was determined by titration with alkali after addition of sodium oxalate to complex the uranium and prevent its precipitation.

The resulting extraction curve, shown in Fig. 2, corresponds closely with other published results[2] for nitric acid alone, except that the observed extraction of nitric acid is uniformly a few per cent lower in presence of uranium. This is to be expected because part of the TBP is combined with the uranium and is not available for nitric acid extraction.

The extraction of uranyl salt into TBP is increased by the presence of the common

[4] T. R. SCOTT, *Analyst*, **74**, 486 (1949).
[5] R. L. MOORE, AECD-3196 (1951).

nitrate ion. However, as shown in Fig. 1, the partition coefficient curve exhibits a maximum at about 6 M nitric acid concentration. SCARGILL *et al.*[6] have indicated that although the salting out effect by the nitrate ion causes the steep rise at the lower acidities, the formation of nitrate complexes and the competition by the nitric

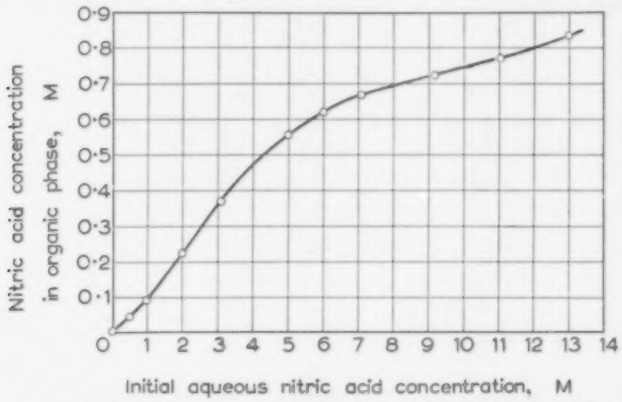

FIG. 2.—Nitric acid extraction into 19 per cent TBP in kerorene during the extraction of uranyl nitrate

acid for the available TBP check the rise at the higher acidities and often cause the partition coefficient to pass through a maximum.

Effect of uranyl nitrate concentration. Extraction of uranyl nitrate solutions of various concentrations containing 6 M nitric acid was carried out with 19 per cent TBP at 20°C. The results are shown in Table 1 where the uranyl nitrate concentration

TABLE 1.—EFFECT OF CONCENTRATION UPON THE EXTRACTION OF URANYL NITRATE

Concentration of $UO_2(NO_3)_2$ (g/l.)	Partition coefficient	Percentage extracted
1·0	60?	98·40
3·0	33·4	97·10
5·0	33·2	97·10
10·0	32·3	97·00
25	30·0	96·75
50	21·0	95·45
100	7·43	88·05
200	1·37	57·80
400	0·44	30·70
650	0·24	19·60

of 650 g/l. represents a saturated solution. These results show that greater than 97 per cent extraction can be obtained at uranyl nitrate concentrations below 10 g/l.

With the TBP-kerosene concentration employed in these experiments the amount of uranyl nitrate which combines with TBP is fixed, since the uranyl nitrate and

[6] H. A. C. MCKAY. *Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, p. 314. United Nations (1956); D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD and H. A. C. MCKAY, *J. inorg. nucl. Chem.* **4**, 304 (1957).

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TBP form a definite compound, $UO_2(NO_3)_2 \cdot 2TBP$, as suggested by MOORE.[5] Therefore, when the concentration of uranyl nitrate is low the content of TBP in kerosene is more than the amount combining with uranyl nitrate and consequently its extraction will be more efficient. When the concentration of uranyl nitrate is increased towards saturation, on the other hand, the partition coefficient rapidly decreases, as shown in Table 1, owing to exhaustion of the available TBP.

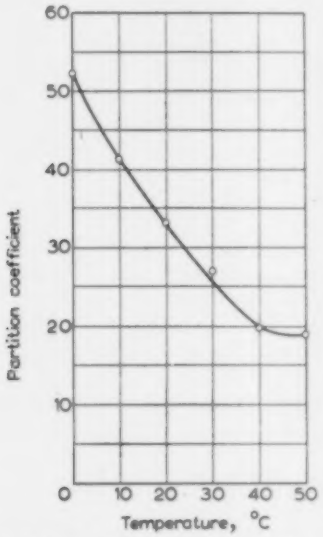

FIG. 3.—Effect of temperature upon the extraction of uranyl nitrate by 19 per cent TBP in kerosene

Effect of temperature of extraction. Extraction of 5 g/l. uranyl nitrate solution containing 6 M nitric acid was carried out with 19 per cent TBP in kerosene at temperatures of 0, 10, 20, 30, 40 and 50°C. The result is shown in Fig. 3.

Fig. 3 shows that when the extraction temperature is low the partition coefficient is large, and that it decreases with increasing temperature. Above 20°C the percentage extraction falls below 97 per cent. It is desirable therefore that the extraction of uranyl nitrate be carried out at less than 20°C.

From the foregoing results the following conclusion is drawn: when a uranyl nitrate solution of less than 10 g/l. concentration containing 6 M nitric acid is extracted with 19 per cent TBP in kerosene at below 20°C, greater than 97 per cent extraction is obtained.

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THE ION-EXCHANGE RESIN ADSORPTION OF THALLIUM(I) AND (III)

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Abstract—The adsorption of small concentrations of radiothallium(III) on the cation-exchange resin Amberlite IR-120(H) begins to decrease at 8 and 32°C when the concentrations of hydrochloric and hydrobromic acids in the solution are about 10^{-3} and 10^{-2} and 10^{-4} and 10^{-3} M respectively. The adsorption of tracer thallium at 25°C on the anion-exchange resin Dowex 1-X8 is at a maximum when the concentration of hydrochloric acid in the solution is about 10^{-1} and 1 M for the (III) and (I) oxidation states respectively. The presence of perchloric acid depresses markedly the adsorption of tracer thallium(III) on Dowex-1 from hydrochloric acid media.

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KRAUS, NELSON and SMITH[1] have studied the anion-exchange resin adsorption of thallium(III) from hydrochloric acid media and BONNER[2] has studied the exchange of thallium(I) with the cation-exchange resin Dowex-50. KRAUS and NELSON[3] have pointed out that a great many chloride complex forming metals show characteristic adsorption maxima on anion-exchange resins. Purposes of the present study included extending the work of KRAUS, NELSON and SMITH[1] to lower chloride concentrations in order to detect the maximum of the thallium(III) adsorption curve and investigating the anion-exchange resin adsorption characteristics of thallium(I).

EXPERIMENTAL

Resin preparation. The Amberlite IR-120(H) was conditioned by repeated alternated washings with 1·0 M NaOH, 6·0 M $HClO_4$, and distilled water and dried at 90°C. The Amberlite IR-4B, a weakly basic anion-exchange resin in the free base form, and the Amberlite IRA-400, a strongly basic anion-exchange resin in the chloride form, were conditioned by repeated washing with distilled water and air dried. The Dowex 1-X8, a strongly basic polystyrene quaternary amine type anion-exchange resin, was cleaned and converted to the chloride (or bromide) form by repeated alternate washings with 6·0 M NaOH, 6·0 M HCl (or HBr), and distilled water and dried at 70°C over "Anhydrone". In order to avoid reduction of thallium(III) by resin impurities, the Dowex-1 was pretreated with chlorine in some of the experiments. This operation must be carried out under acid conditions and the resin thus treated not subsequently treated with base since some Hofmann degradation occurs even after repeated washing.

Materials, experimental conditions and procedures. The Amberlite studies were conducted at 7·9 ± 0·1, 20·1 ± 0·1, and 31·8 ± 0·2°C, and the ionic strength and acidity were maintained at 0·5 M by the addition of $HClO_4$. The concentration of thallium(III) in these experiments was about 7×10^{-5} M, and its stock solution was prepared by the electrolytic oxidation on a platinum electrode of a thallium(I) perchlorate solution. The latter solution was prepared by fuming a 4 year ^{204}Tl nitrate

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[1] K. A. KRAUS, F. NELSON and G. W. SMITH, *J. phys. Chem.* **58**, 11 (1954).
[2] O. D. BONNER, *J. phys. Chem.* **58**, 719 (1955).
[3] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Paper 837. United Nations (1956).

solution, obtained from Oak Ridge, with $HClO_4$. The thallium(III) perchlorate stock solution, about 3 M in $HClO_4$, was analysed at regular intervals over a three month period by Dr. R. W. STOENNER of Brookhaven and reduction amounted to less than 0·3 per cent. The experimental batches, containing 0·50 g resin and 15 ml solution, were equilibrated by mechanical shaking in a thermostatically controlled bath for 72 hr or longer. Five millilitre aliquots of the supernatant solution were removed, diluted up to 25 ml, and counted in a liquid Geiger counter. CARPENTER[4] has found that the bromide catalysis of the thallium(I)–thallium(III) electron exchange reaction is photosensitive, however, experiments in blackened vessels indicated that the present experiments are not light sensitive.

The Dowex-1 studies were conducted at 25·1 ± 0·2°C, and the ionic strength and acidity were allowed to vary with the changing halide concentration. The 12 day ^{200}Tl, in trace amounts with no added carrier, was prepared in the M.I.T. cyclotron by a $(d, 2n)$ reaction on a HgO target. The

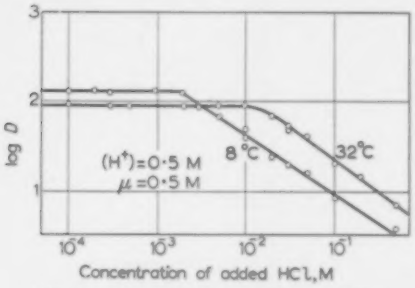

FIG. 1.—The adsorption of thallium(III) on Amberlite IR-120(H) from aqueous hydrochloric acid solutions of ionic strength 0·5.

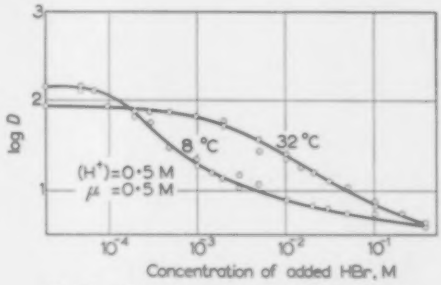

FIG. 2.—The adsorption of thallium(III) on Amberlite IR-120(H) from aqueous hydrobromic acid solutions of ionic strength 0·5.

radiothallium was separated and purified by a procedure described by BOGAR and IRVINE[5] which involves solvent extraction of the thallium(III) from chlorine-saturated 6·0M HCl solution into bis(2-chloroethyl) ether. The radiothallium(I) solutions were prepared by reducing thallium(III) by prolonged boiling or SO_2 treatment followed by boiling. In these experiments the batches contained 0·01 or 0·10 g resin and 10, 100 or 200 ml solution. Four millilitres aliquots of the supernatant solution were transferred to small vials and counted in a well-type γ-scintillation counter. Reduction of thallium(III) and oxidation of thallium(I) were commonly encountered difficulties. At small chloride concentrations the former cannot be remedied by the presence of chlorine since this significantly perturbs the chloride concentration, and the latter cannot be eliminated by the presence of SO_2 since, again, extraneous complexing anions, presumably HSO_3^-, are introduced which give rise to anomalously high adsorption. The use of chlorine pretreated resin was only partially effective in preventing the reduction of thallium(III). As a consequence of these difficulties the thallium(III) adsorption curve (Fig. 4) represents the maximum and the thallium(I) curve (Fig. 4) the minimum values of sets of data, the points plotted representing about 30 per cent of the total number of measurements. The susceptibility of thallium(III) to reduction decreases markedly as the concentration of HCl increases, presumably because of stabilization of that oxidation state by complex formation.

The correction for resin swelling was found to be small and hence was not included in the calculation of the distribution coefficients, D

$$D = \frac{\text{(vol. of soln. in ml) (radioactivity in the resin)}}{\text{(wt. of resin in g) (radioactivity in the soln.)}}. \qquad (1)$$

RESULTS AND DISCUSSION

Cation exchange. The adsorption of thallium(III) on Amberlite IR-120(H) from hydrochloric and hydrobromic acid solutions at 8 and 32°C is shown in Figs. 1 and 2.

[4] L. G. CARPENTER, Ph.D. Thesis, Columbia University (1956).
[5] L. C. BOGAR and J. W. IRVINE, Jr., *M.I.T. Lab. Nucl. Sci. Progress Report* p. 5 (1954).

In perchlorate media, in the absence of an added complexing anion, even in solutions 0·5 M in H^+, approximately 20 per cent of the thallium(III) is not retained by the resin. This result suggests either that (a) the adsorption coefficient is small, being comparable to that for indium(III)[6] but considerably less than that reported for trivalent cerium on Dowex-50,[7] or that (b) hydrolysis has reduced the concentrations of highly charged and hence strongly adsorbing cationic species. For data obtained in the absence of added complexing anions, interpreting D as an equilibrium constant and plotting its logarithm vs. the reciprocal of 281, 293 and 305°K a straight line is obtained with a slope corresponding to −3·4 kcal/mole deg. Desorption begins to occur at smaller concentrations of bromide ion than of chloride ion (Figs. 1 and 2) indicating that thallium(III) bromide complexes are stronger than the corresponding chloride complexes, a conclusion reached by CARLESON and IRVING.[8] At 8, 20 and 32°C and an acidity of 0·5 M, thallium(III) is no less strongly adsorbed on Amerlite IR-120(H) in the presence of added $1{\cdot}30 \times 10^{-2}$ M NaCN or of $3{\cdot}17 \times 10^{-2}$ M NaF than in their absence.

Anion exchange. At 8, 20 and 32°C 85, 71, and 44 per cent of the thallium(III) is adsorbed on Amberlite IRA-400 even in the absence of added halide ion. This effect is of greater magnitude and shows a different temperature dependence than the non-adsorption on Amberlite LR-120(H), and may not, therefore, be attributable to hydrolysis. In HBr the adsorption of thallium(III) on Amberlite IRA-400 begins to increase when the bromide concentration is 10^{-4} to 10^{-3} M, in HCl 10^{-3} to 10^{-2} M, as might be expected from the cation exchange curves in Figs. 1 and 2. Thallium(III) does not begin to adsorb strongly on Amberlite IR-4B until the halide concentration is greater than 0·10 M.

At low concentrations of HCl thallium(I) and (III) exhibit anomalously high adsorption on Dowex-1 and the adsorption coefficient, D, is not independent of resin weight. Experiments with glass wool indicated that these difficulties are due to surface adsorption. In Table 1, A is the ratio of thallium radioactivity in an

TABLE 1.—GLASS ADSORPTION AT 25°C

Oxidation state of thallium	Concentration of HCl, (M)	A
3	10^{-4}	1·45
3	10^{-3}	1·15
3	10^{-2}	1·00
3	10^{-1}	1·00
3	3	1·00
1	10^{-4}	1·08
1	10^{-3}	1·00
1	10^{-2}	1·00
1	10^{-1}	1·00

[6] J. A. SCHUFLE and H. M. EILAND, *J. Amer. chem. Soc.* **76**, 960 (1954).
[7] J. A. MARINSKY, *M.I.T. Lab. Nucl. Sci., Tech. Report No.* 34 (1949).
[8] B. G. F. CARLESON and H. IRVING, *J. chem. Soc.* 4390 (1954).

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1·0 M HCl solution in the absence of glass wool to the activity of a solution of acidity specified in the presence of 0·20 g of glass wool.

The presence of perchlorate ion depresses markedly the adsorption of thallium(I) and (III) on Dowex-1 from HCl and HBr solutions (Fig. 3). Perchlorate ion adsorbs strongly on this anion-exchange resin[9] thus competing with the anionic thallium complexes in the ionic equilibria involved. It is of interest to notice that the solvent extraction of thallium(III) into bis(2-chloroethyl) ether from aqueous HCl is also depressed by the presence of perchloric acid.[10,11]

Fig. 4 shows the adsorption of thallium(I) and (III) from aqueous HCl solutions

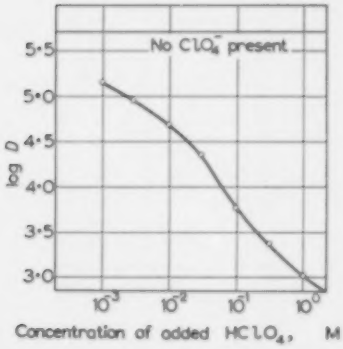

FIG. 3.—The effect of perchlorate ion on the absorption of tracer thallium(III) on Dowex 1-X8 chloride from 1·0 M hydrochloric acid solution at 25°C.

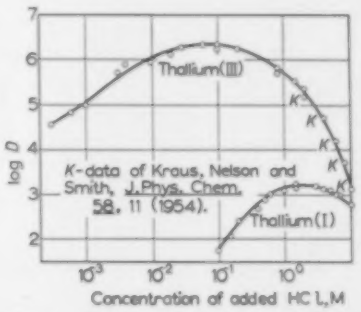

FIG. 4.—The adsorption of tracer thallium(I) and (III) on Dowex 1-X8 chloride from aqueous hydrochloric acid solutions at 25°C.

on Dowex 1-X8 chloride at 25°C. This work represents an extension of that of KRAUS, NELSON and SMITH[1] to lower chloride concentrations and for thallium(I) as well. The adsorption of thallium(III) from HBr media was too strong to be reliably measured under present experimental circumstances, while the adsorption of thallium (I) from HBr media was not reproducible, extensive oxidation being indicated.

FRONAEUS,[12] SCHUBERT and LINDENBAUM,[13] SCHUFLE and EILAND,[6] and CARLESON and IRVING[8] have developed methods for evaluating the formation constants of the complex ions of metals from their cation-exchange resin adsorption behaviour; while FOMIN *et al.*[14] and CORYELL and MARCUS[15] have elaborated methods for obtaining this same information from anion-exchange resin adsorption data. Because of the strength of the thallium(III) chloro-complexes the change in the solution anion concentration due to removal by complex-formation is not negligible, and hence the comparatively simple methods of interpreting cation-exchange behaviour mentioned above are not applicable. However, if the assumptions are made that (a) TlA_n^{3-n} is adsorbed very strongly and TlA_{n-1}^{4-n} very weakly, that (b) they are the only species present in significant concentrations, and that (c) D is equal to half of the initial D when the concentrations of these two species are equal, then the formation constant of the complex TlA_n^{3-n} may be crudely approximated from the relation.

$$K_{TlA_n^{3-n}} = (TlA_n^{3-n})/(TlA_{n-1}^{4-n})(A^-) \approx \frac{\text{(radioactivity in resin)}}{(A^-)\text{(radioactivity in soln.)}}. \qquad (2)$$

[9] G. E. BOYD and B. A. SOLDANO, *Z. Elektrochem.* **57**, 162 (1953).
[10] R. H. HERBER, W. E. BENNETT, D. R. BENTZ, L. C. BOGAR, R. J. DIETZ, G. S. GOLDEN and J. W. IRVINE, JR., 126th Meeting, Amer. Chem. Soc., New York, N.Y. Abs. P–79 (1954).
[11] D. L. HORROCKS and A. F. VOIGT, *J. Amer. chem. Soc.* **79**, 2440 (1957).
[12] S. FRONAEUS, *Acta chem. scand.* **5**, 859 (1951).
[13] J. SCHUBERT and A. LINDENBAUM, *J. Amer. chem. Soc.* **74**, 3529 (1952).
[14] V. V. FOMIN, L. N. FEDOTOVA, V. V. SIN'KOVSKII and M. A. ANDREEVA, *Zh. fiz. khim.* **29**, 2042 (1955).
[15] C. D. CORYELL and Y. MARCUS, *Bull. Res. Council Israel* **4**, 7 (1954).

TABLE 2.—FORMATION CONSTANTS OF THE COMPLEXES OF THALLIUM(I) AND (III)

Complex	Formation constant	Temp. (°C)	Ionic strength	Reference
$Tl(OH)_n^{3-n}$	$1{\cdot}6 \times 10^{14}$	20·0	0·5	Method A
$TlOH^{++}$	6×10^{14}			1, 2, 3,
$TlOH^{++}$	ca. 10^{-1}			4, 5
$Tl(CN)_n^{3-n}$	$<10^{11}$	8–32	0·5	Method A
	$n = 3,4$ exist in solution			6
TlF_n^{3-n}	$<10^{4}$	8–32	0·5	Method A
TlF_3	$<10^{4}$			7
$TlBr_n^{3-n}$	$6{\cdot}7 \times 10^{3}$	8	0·5	Method A
	$2{\cdot}2 \times 10^{2}$	32	0·5	Method A
$TlBr^{++}$	5×10^{9}	18(?)	0·0	8
	8×10^{8}	21	1·2	9
$TlBr_2^{+}$	8×10^{6}	18 ?)	0·0	8
	3×10^{7}	21	1·2	9
$TlBr_3$	4×10^{6}	18(?)	0·0	8
	5×10^{5}	21	1·2	9
$TlBr_4^{-}$	5×10^{2}	18(?)	0·0	8
	1×10^{4}	21	1·2	9
$TlCl_n^{3-n}$	$2{\cdot}0 \times 10^{2}$	8	0·5	Method A
	$2{\cdot}5 \times 10^{1}$	32	0·5	Method A
$TlCl^{++}$	$1{\cdot}3 \times 10^{8}$	18(?)	0·0	8
	$1{\cdot}8 \times 10^{8}$	21	1·2	9
$TlCl_2^{+}$	3×10^{5}	18(?)	0·0	8
	$1{\cdot}4 \times 10^{5}$	21	1·2	9
	$1{\cdot}1 \times 10^{3}$	25	0·0	Method B
$TlCl_3$	$1{\cdot}6 \times 10^{2}$	18(?)	0·0	8
	$1{\cdot}3 \times 10^{3}$	21	1·2	9
	$1{\cdot}2 \times 10^{2}$	25	0·0	Method B
$TlCl_4^{-}$	3×10^{2}	21	1·2	9
	3·3	25	0·0	Method B
TlCl	3·2	18	—	10
	3·3	18	—	11
	3·3	21	0·0	9
	4·0	25	0·0	12
	7	25	4	13
	2·9	25	0·0	Method C
$TlCl_2^{-}$	0·37	25	—	12
	2·5	25	4	13
	0·33	25	0·0	Method C
$TlCl_3^{=}$	1·1	25	4	13
	(0·13)	25	0·0	Method C

1. G. HARBOTTLE and R. W. DODSON, *J. Amer. chem. Soc.* **73**, 2442 (1951).
2. C. JOHNSON, *J. Amer. chem. Soc.* **74**, 959 (1952).
3. R. W. DODSON, *J. Amer. chem. Soc.* **75**, 1795 (1953).
4. M. S. SHERRILL and A. J. HAAS, JR., *J. Amer. chem. Soc.* **58**, 953 (1936).
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7. B. G. F. CARLESON and H. IRVING, *J. chem. Soc.* 4390 (1954).
8. R. BENOIT, *Bull. soc. chim. Fr.* **16**, 518 (1949).
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10. L. ONSAGER, *Phys. Z.* **28**, 277 (1927).
11. C. W. DAVIS, *Trans. Faraday Soc.* **23**, 354 (1927).
12. K. H. HU and A. B. SCOTT, *J. Amer. chem. Soc.* **77**, 1380 (1955).
13. R. O. NILSSON, *Ark. Kemi* **10**, 363 (1957).

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This will be called Method A. An attempt was also made to interpret the anion-exchange resin data by the method of CORYELL and MARCUS[15] (Method B). At HCl concentrations greater than 1·0 M invasion of the resin phase by solution electrolyte becomes significant and it becomes necessary to consider an invasion correction when applying this method (Method C). The results of interpreting the present data by these three methods, together with values reported previously in the literature, are summarized in Table 2. CORYELL and MARCUS[15] have pointed out that their method is most accurate for calculating the formation constants of neutral complexes, and, indeed, the value for $TlCl_3$ evaluated by Method B is in good agreement with the results of Benoit. The values for the formation constants of the chloride complexes of thallium(I) calculated by Method C also appear to be in agreement with previously reported values.

Acknowledgements—I wish to acknowledge the many valuable suggestions and assistance of Prof. R. W. DODSON of Columbia University and Brookhaven National Laboratory, Profs. C. D. CORYELL and J. W. IRVINE, JR. of the Massachusetts Institute of Technology, and Dr. Y. MARCUS of the Israel Ministry of Defence and my gratitude for facilities and funds supplied by the United States Atomic Energy Commission.

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J. Inorg. Nucl. Chem., 1958, Vol. 6, pp. 344 to 346. Pergamon Press Ltd., London

LETTERS TO THE EDITOR

The stoicheiometry of MnTe

(*Received* 16 *December* 1957)

AN ATTEMPT to define the stoicheiometry and phase boundaries in the system Mn–Te by X-ray methods has been reported by FURBERG.[1] The homogeneity range in the compound MnTe, was reported to be too small to be detected by X-ray methods.

Because of the interesting electrical and magnetic properties of the compound MnTe, it was desired to obtain more information about the dependence of these properties on composition, so the question of stoicheiometry of MnTe was re-examined.

EXPERIMENTAL

Materials. The preparation of the compounds was made using highest purity electrolytic manganese which was vacuum distilled to give about 0·01 per cent metallic impurities and about 0·03 per cent gaseous impurities (principally oxygen). Thus, a total manganese content of 99·96 per cent was obtained. The tellurium was used as furnished and was indicated by the supplier to be 99·99 per cent tellurium.

Preparation. The stoicheiometry of MnTe was examined in the following fashion: $MnTe_{1\cdot1}$ was prepared by reacting the required amounts of carefully weighed and mixed manganese and tellurium. The mixed powders (ground to pass 60 mesh) were sealed in evacuated Vycor ampoules and heated slowly to 700°C and held for 24 hr. The $MnTe_{1\cdot1}$ preparation was then made one part of a two part system of which the other part was manganese powder in approximately tenfold excess over that required to react with the excess tellurium represented in $MnTe_{1\cdot1}$. Variation of the amount of excess manganese gave results consistent with those reported below. This excess of manganese was used to insure that the equilibrium concentration of tellurium in the compound would be the minimum. (This kind of reaction using excess manganese will be called Type I.) The two boats were sealed in evacuated Vycor and held at 800°C for 48 hr—a time found by experiment to give constant weight in each boat—then air quenched. The tube was opened and the boats were weighed to find the weight of tellurium transferred. From the weight transferred, it was possible to calculate the concentration of tellurium in $MnTe_{1\pm x}$. A series of these experiments gave the average value of x to be 0·002 $\pm$ 0·0005 and with positive sign.

A second series of experiments was designed to seek evidence for a homogeneity range from $MnTe_{1+x}$ to $MnTe_{1+y}$ (where y is greater than x). A previously prepared weighed quantity of $MnTe_{0\cdot9}$ was placed in a boat and sealed in evacuated Vycor with another boat containing a previously prepared weighed quantity of $MnTe_{1\cdot5}$. The amount of tellurium available in $MnTe_{1\cdot5}$ to bring the $MnTe_{0\cdot9}$ to MnTe was about twice that required by stoicheiometry so that any tendency for the formation of the tellurium-excess compound $MnTe_{1+y}$ could proceed. (This reaction with tellurium excess will be called Type II.) The tubes were heated to 800°C, held for 48 hr, and air quenched. By determining the gain in weight of the $MnTe_{0\cdot9}$ boat, it was possible to calculate the equilibrium concentration of tellurium in $MnTe_{1+y}$. The average of value y was found to be 0·013 $\pm$ 0·003.

Examination. The materials produced in these reactions have been subjected to X-ray examination and to thermoelectric power measurements. Type I material was found to be single phase MnTe,

[1] S. FURBERG, *Acta. chem. scand.* **7**, 693 (1953).

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and Type II material was found to be MnTe plus $MnTe_2$. Thermoelectric measurements gave for Type I an average value of 572 ± 6 μV/deg. and for Type II an average value of 573 ± 8 μV/deg. (both values for 50°C). The striking agreement between the two types was unexpected. There was a remarkable uniformity in values found within the types as well. When the as-sintered materials from the Type I and Type II reactions were finely ground, pelleted and the thermoelectric power measured, the average values dropped to 338 ± 5 μV/deg. and 364 ± 4 μV/deg. respectively (at 50°C).

DISCUSSION

The purely chemical evidence would indicate that MnTe exists as an excess tellurium compound in the homogeneity range of $MnTe_{1\cdot002}$ to $MnTe_{1\cdot012}$ at 800°C. However, there are difficulties in connection with this result. It will be noted that the level of excess tellurium content in the final product is less than the observed impurity level of the starting materials. The presence of impurities which makes some manganese unavailable for reaction with the tellurium would lead to calculated errors in the tellurium content of the MnTe phase. In view of this, the stated values of x and y should be considered lower limits. Since the principal impurity is oxygen, calculations were made to find what correction 0·03 wt. per cent oxygen would require. In one Type I experiment the uncorrected value of $MnTe_{1\cdot0056}$ was found. By considering the oxygen to be present as gas, the stoicheiometry was shifted to $MnTe_{1\cdot0058}$ and by considering the oxygen to be present as MnO (the most likely probability) the result became $MnTe_{1\cdot021}$. Since there is no knowledge of the exact form of the oxygen in the vacuum melted manganese, no final estimate of this effect can be made.

Due to the prolonged reaction times at high temperatures, a slight attack of the Vycor bulbs used as boats was noted, and the possibility of some reaction of MnTe with silica cannot be excluded. It might be assumed that the MnTe would be oxidized giving some manganese silicate while liberating tellurium.

In addition, several assumptions were made regarding the equilibrium reactions of Types I and II, namely, that compositions with a higher tellurium content would have a higher vapour-pressure of tellurium than those with lower tellurium content; and that no manganese is transferred in any fashion. Whether these assumptions were completely reliable is still not certain.

The presence of $MnTe_2$ in the product from the Type II reaction may indicate that a genuine homogeneity range does not exist, or it may be interpreted that, due to inability to quench effectively, $MnTe_2$ precipitates from a wider solubility region in MnTe at 800°C to form a two phase region at room temperature. At any rate, the existence of a homogeneity range in MnTe at room temperature remains highly questionable.

The thermoelectric data imply that: (1) the composition of both Type I and Type II materials is nonuniform because the thermoelectric power changes upon grinding and (2) the composition of the intergranular material in both types must be nearly identical. Since the grinding of a homogeneous material should not affect the thermoelectric power measurement, it must be concluded that the thermoelectric power that is measured in the as-reacted state for both Type I and Type II is not representative of the bulk composition. It has been suggested that a film of tellurium-rich material covers the individual particles and cements them together. This film would be broken during grinding and the thermoelectric power of the bulk material would then be observed.

To sum up: MnTe appears to be an excess tellurium compound and the excess is of the order of $MnTe_{1\cdot002}$ to $MnTe_{1\cdot012}$ at 800°C. The homogeneity range, if it exists at all, must be extremely limited at room temperature. The exact nature of the compound which gives the thermoelectric value of MnTe is still in doubt.

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The half-life of ^{139}Ba

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DURING recent investigations of the proton-induced fission of the actinide elements it was observed that the half-life of ^{139}Ba was shorter than the accepted value of 85 min. Since this constant has never been determined accurately,[1–4] and as ^{139}Ba is frequently used as a reference nuclide in fission studies, a further measurement of this half-life was considered worthwhile.

Samples of ^{139}Ba were prepared by three methods: by (n, γ) reaction on Matthey "Specpure" $BaCO_3$; by thermal neutron fission of pure uranium metal and by the fission of uranium by 35 MeV protons. The irradiated samples were dissolved in hydrochloric acid which contained barium carrier. The barium was purified by several ferric hydroxide scavenges and by precipitations as $BaCl_2$ in HCl–ether mixture. It was finally precipitated for counting as $BaSO_4$, and a decay curve was taken in a 2π methane proportional counter. The contaminating activity in the sample prepared by the reaction Ba(n, γ) was mainly 29 hr ^{135}Ba which amounted to about 0·1 per cent of the initial activity. The ^{139}Ba obtained from fission was contaminated with ^{140}Ba–^{140}La and an almost negligible amount of ^{141}Ba–^{141}La. The activity from the mass chain 141 was reduced to a very small quantity (about 0·3 per cent of the ^{139}Ba) by performing the final La–Ba separation 200 min after the end of the irradiation thus allowing most of the 18 min ^{141}Ba to decay to ^{141}La.

A summary of a weighted least squares fit of the decay curves corrected for the long-lived contaminants is given in the table below. The errors quoted are the standard deviations.

Method of preparation	Number of half-lives observed	Half-life (min)
Ba(n, γ)	10·2	82·90 ± 0·05
Ba(n, γ)	8·8	82·76 ± 0·08
Ba(n, γ)	9·2	82·90 ± 0·05
U(n, f)	6·4	82·89 ± 0·16
U(p, f)	5·9	82·75 ± 0·18

Considering possible systematic errors we propose a value of 82·9 min for the half-life of ^{139}Ba with an estimated error of ±0·1 min.

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[1] C. R. DILLARD, H. FINSTON and R. M. ADAMS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) Div. IV, Vol. 9, p. 1101. McGraw-Hill, New York (1951).
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[3] L. R. SHEPHERD and J. M. HILL, *Nature, Lond.* **162,** 566 (1948).
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ANNOUNCEMENT

ABSTRACTS for papers to be presented at the Seventh Conference on Hot Laboratories and Equipment to be held in Cleveland, Ohio, April, 1959, are due 15 September 1958 and should be sent to programme chairman: L. G. STANG, JR., Brookhaven National Laboratory, Upton, Long Island, New York. Deadline for papers will be announced later. Papers are invited on all phases of hot laboratories and equipment for handling radioactive material including design, construction, operation, maintenance, decontamination, remodelling, shielding calculations, costs, etc.

Papers to be published in future issues

C. H. SHIFLETT, M. E. STEIDLITZ, F. D. ROSEN and W. DAVIS, JR.: The chemical effect of alpha particles on uranium hexafluoride.

J. A. BROTHERS, R. G. HART and W. G. MATHERS: The nitrate complexes of tetravalent plutonium.

G. HERRMANN: Über die elektrolytische Abscheidung von träger freiem Strontium aus wässriger Lösung.

I. KALNINS and G. GIBSON: The interaction of uranium tetrachloride with hydrazine ammonia and amines.

R. E. MCCARLEY, D. S. MARTIN, JR. and L. T. COX: Solid state and solution exchange of platinum between $[Pt(en)Br_4]$ and $[Pt(en)Br_2]$.

J. FAHLAND, G. HERRMAN und F. STRASSMAN: Zur Kinetik der elektrochemischen Abscheidung radioaktiver Ionenarten auf Metallober flächen.

E. G. PROUT: The thermal decomposition of irradiated potassium permanganate.

J. MALY and V. VESELÝ: A contribution to sodium polyuranate chemistry.

J. LEWIS, R. J. IRVING and G. WILKINSON: Infra-red spectra of transition metal–nitric oxide complexes—I. Complexes involving donation from the NO^+ ion.

R. CONSTANT: Production de ^{131}I sans porteur à partir d'acide tellurique.

G. PILCHER and H. A. SKINNER: Valence-states in titanium and vanadium.

D. P. GRADDON: The absorption spectra of complex salts—II. Cupric complexes with dicarboxylic acids.

J. JACH and N. SUTIN: The Szilard–Chalmers reaction in ferricinium picrate.

W. W. WENDLANDT: The thermal decomposition of yttrium and the rare earth metal sulphate hydrates.

K. S. TOTH: A new holmium activity, ^{150}Ho.

J. D. BUCHANAN: Radiochemical procedure for beryllium.

G. W. WATT and L. VASKA: The interaction of ammonium and potassium hexabromoösmate (IV) and liquid ammonia at -34 and $90°$.

D. C. WILLIAMS and S. KATCOFF: Branching in the decay of ^{97}Ru to ^{97m}Tc and ^{97}Tc.

F. J. JOHNSTON, D. A. HUTCHINSON and J. J. KATZ: Oxygen exchange between uranium oxides and water.

R. A. PENNEMAN and E. STARITZKY: Preparation and properties of $LiAu(CN)_2$, $NaAu(CN)_2$ and the double compound $LiAu(CN)_2 \cdot KAu(CN)_2$.

J. C. WALLMAN, P. GRAF and L. GODA: The specific activities and half-lives of americium-241 and americium-243.

D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. S. SIRONEN: Acidic esters of *ortho*-phosphoric acid as selective extractants for metallic cations. Tracer studies.

C. J. HARDY, D. SCARGILL and J. M. FLETCHER: Studies on protactinium V in nitric acid solutions.

D. C. WILLIAMS and S. KATCOFF: Neutron activation cross-sections of ^{96}Ru and ^{102}Ru.

F. H. CRIPPS and J. W. WEALE: A new method for the absolute counting of ^{239}Np.

A. G. GOBLE and A. G. MADDOCK: Protactinium—III. Solvent extraction from halide solutions.

L. B. ASPREY and T. K. KEENAN: Tetravalent americium and curium; The absorption spectra of the tri- and tetra-fluorides of these elements.

J. E. EDWARDS: Half-lives of ^{201}Ti and ^{134}Cs.

G. A. OLAH, A. E. PAVLATH and S. J. KUHN: Note on the preparation of iodine pentafluoride.

W. P. GRIFFITH, J. LEWIS and G. WILKINSON: Infra-red spectra of transition metal–nitric oxide complexes—II. Complexes involving the NO^- ion.

B. M. FOREMAN, JR. and G. T. SEABORG: Nuclear thermodynamics of the heaviest elements—II.

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R. C. YOUNG: Investigation of the black solid formed on reaction of uranium metal with hydrochloric acid.

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G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—I. Konduktometrische Titrationen in geschmolzenem Acetamid.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—II. EMK-Messungen und potentiometrische Titrationen in geschmolzenem Acetamid.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—III. Letifahigkeit und Stärke von Elektroylten in geschmolzenem Acetamid.

J. H. FREEMAN and M. L. SMITH: The preparation of anhydrous inorganic chlorides by dehydration with thionyl nitrate.

J. HALPERIN, J. O. OLIVER and H. S. POMERANCE: The thermal neutron absorption cross-section of ^{240}Pu.

F. A. COTTON and J. W. GEORGE: Properties of SF_4 and its adduct with BF_3.

A. A. WOOLF: The preparation of rhenium from iodo compounds.

F. M. BREWER, G. GARTON and D. M. L. GOODGAME: The preparation and crystal structure of gallium trifluoride.

A. J. ZIELEN, J. C. SULLIVAN and D. COHEN: The photochemical reduction and the autoreduction of neptunium(VI).

D. F. PEPPARD, J. R. FERRARO and G. W. MASON: Hydrogen bonding in organophosphoric acids.

G. R. CHOPPIN and S. G. THOMPSON: Electron capture half-life of ^{245}Cm.

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